MATHEMATICAL AND THEORETICAL PHYSICS

Volume II

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MATHEMATICAL AND THEORETICAL PHYSICS

Volume II

EGIL A. HYLLERAAS

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Acknowledgment

When the wish for an English edition of Egil A. Hylleraas' treatise on *Mathematical and Theoretical Physics* was first expressed to his family, we immediately understood that without the aid of skilled and able people, there was nothing we could do to prepare such an edition.

Therefore I want to express my warmest thanks to the two persons at the Physics Department of the University of Oslo, Norway, who have made this English edition possible, namely to my father's friend and colleague *försteamanuensis* John Midtdal, who, with his thorough knowledge of my father's works, has given invaluable help and advice in the preparation of this edition, and to *cand. real.* Andreas Quale, who at present holds a University Fellowship here in Oslo and, with his combined knowledge of physics and of the English language, willingly and fearlessly undertook the great work of translating that half of the treatise which my father had not translated himself, as well as to do the author's proofreading of the entire work. For all this I am very grateful.

And I also wish to extend my thanks to all those people who in different ways have been involved in the making of this book, and who with their initiative, their conscientiousness, and their workmanship have contributed to make this English edition what my father hoped it would be.

Oslo, Norway
July 1969

INGER HYLLERAAS BÖ

Foreword

Egil A. Hylleraas was a very forthright, humble man with a very keen analytical mind. In common with such physicists as Einstein and Feynman, he was gifted with exceptional physical intuition. Most of the techniques that we now use in molecular quantum mechanics were conceived by Hylleraas. To him, mathematics was a tool for solving physical problems. However, he spent long hours in trying to find the most direct mathematical approach. When he found a "cute" mathematical trick that simplified the treatment, he was as delighted as a child with a new toy.

In this book, he explains in his own simple but elegant fashion the development of theoretical physics. At each step he derives the mathematics most appropriate for the solution of the physical problem under consideration. And with his sly sense of humor, he occasionally adds a historical tidbit which makes the treatment more interesting. Many of the derivations are quite novel, others were standard fifty years ago but have long since been forgotten. All of his derivations are neat, simple, and self contained; yet they are completely rigorous. In reading this book, the reader cannot help being carried away with Hylleraas' joy in discovering physics. Primarily the treatment is directed at beginning graduate students in physics. However, because of the clever methods that Hylleraas employs and his down-to-earth approach to difficult problems, this book is of interest to physicists of all degrees of experience and background.

The first edition of *Mathematical and Theoretical Physics* was published in Norwegian and served as the basis for a sequence of graduate courses that Professor Hylleraas taught at the University of Oslo, and was regarded as the "Bible" by a whole generation of Norwegian physicists. Hylleraas gave me a copy when he came to spend the year 1962–1963 at the University of Wisconsin. Although I can barely read Norwegian, I discovered in this text a myriad of simple derivations and important theorems that are difficult to find anywhere else. I then persuaded Hylleraas to bring this work up to date and to translate it into English. At the time of his death, he had completed

about half of the manuscript. Professor John Midtdal, a former student and for many years a close colleague of Professor Hylleraas at the University of Oslo, brought the remainder of the text up to date by making use of Hylleraas' lecture notes. University Fellow Andreas Quale of the University of Oslo translated this material. Midtdal and Quale, as well as Hylleraas' other students who participated in this project, are to be complimented on the excellence of this new English edition!

Because of its wealth of simple appropriate problems illustrating each point, *Mathematical and Theoretical Physics* is an excellent text. It could be used, as in Norway, to teach a whole sequence of graduate courses covering most aspects of theoretical physics. Or, it could be used to teach individual courses in each of the following areas: The Mathematical Preparations for Theoretical Physics; Classical Mechanics; Thermodynamics, Kinetic Theory of Gases, and Statistical Mechanics; Electricity and Magnetism; and Elementary and Advanced Quantum Mechanics.

1. *Mathematical Preparations for Theoretical Physics.* The subject material for this section of the book is very carefully chosen so as to be useful in many different branches of physics. I suppose that this part should be compared with Morse and Feshbach's treatise on the *Methods of Theoretical Physics.* However, Hylleraas has condensed his treatment to 208 pages, whereas Morse and Feshbach require two volumes of 1975 pages. This section begins with a thorough treatment of vectors and vector fields which includes a good discussion of various types of discontinuous vector fields. Then follow vector transformations and the properties of tensors, orthogonal and nonorthogonal coordinate systems, determinants and their evaluations, matrix algebra, quadratic forms, and their eigenvalues and invariants. The vector space is then generalized to infinite dimensions, which of course leads to expansions of functions in orthogonal polynomials and the concept of completeness. The logical sequence continues with a good discussion of the calculus of variations (with lots of examples), Euler's differential equations of a variational integral, eigenvalue problems and how they are solved, the distribution of eigenvalues, and the completeness of solutions to an eigenvalue equation. The remainder of this section of the book is concerned with the theory of functions: analytic functions, convergence and analytic continuation of power series, contour integrals, the gamma and delta functions and solution of differential equations by power series (stressing the effects of various types of singular points). Finally Hylleraas considers the hypergeometric and Bessel functions, giving the generating functions, integral representations, special cases, and so forth.

2. *Classical Mechanics.* This section begins with a discussion of trajectory and oscillation problems. The treatment of Lagrangian and Hamiltonian

mechanics is truly excellent and contains applications to relativistic electromagnetic problems. The chapter on the motion of solid bodies has a particularly good section on the coefficients of elasticity. The chapter on hydrodynamics provides a very complete treatment of ideal fluids, including conformal mappings of a two-dimensional flow, gravity waves, and the theory of sound. The motion of a sphere through a viscous fluid, and the flow of a viscous fluid through a pipe are also considered.

3. *Thermodynamics, Kinetic Theory of Gases, and Statistical Mechanics.* The treatment of thermodynamics is simple, concise, and appears rather standard. The kinetic theory of gases is presented from the Jeans or Maxwell point of view. Classical and quantum statistical mechanics are explained in a simple fashion. This section ends with a very interesting set of applications of quantum statistics to gas kinetics: the photon gas and the law of radiation, the virial theorem in quantum statistics, sums of states in quantum statistics, ideal gases with weak degeneracy and strong degeneracy of both a Bose-Einstein and a Fermi gas.

4. *Electricity and Magnetism.* The treatment of electrostatics is very complete with many examples, including multipoles, dipole layers, charged spheres, and disks. The dielectric constant is explained in the usual way in terms of a spherical cavity. The Maxwell stress tensor, the field energy in dielectrics, and Kelvin's theorem of minimum energy are given. The section on electrostatics is concluded with a discussion of various types of condensers, the electric balance, and the quadrant electrometer. Magnetostatics is treated in very much the same way as electrostatics. Measurements of magnetic moments and field strengths are discussed. The vector potential is introduced, and the equivalence of the line vortex to the magnetic double layer is noted. After examining the basic laws of electromagnetism, Hylleraas considers the reactive forces, the forces on moving charges, and the mutual potential energy of current-carrying circuits. This leads to a discussion of magnetic field energy, Maxwell's displacement current, and energy transport by radiation. This in turn leads to the mechanical properties of radiation. With respect to the units used in electromagnetism, Hylleraas explains with his sense of humor and knowledge of history exactly how such a sad situation could have arisen. This part of the book concludes with a brilliant treatment of electromagnetic radiation. He starts with a very thorough discussion of Hertzian dipoles and multipole radiation. He shows how to solve the inhomogeneous wave equations, making use of the spectral distribution of the wave function and Green's function in four dimensions. This leads to the Lienard-Wiechert potentials, and finally to a discussion of Cherenkov radiation.

5. *Elementary and Advanced Quantum Mechanics.* Since Hylleraas is one of the fathers of quantum mechanics as we know it today, this part of the book is especially interesting and full of historical reminiscences. He starts with a thorough discussion of blackbody radiation, heat capacity of solids, the photoelectric effect and the Compton effects, and shows how the experimental facts molded the theoretical concepts. His treatment of the Bohr atomic theory is the most thorough and complete which I have ever seen. It makes one wonder how much of this old work might be made use of in connection with modern quantum mechanics. I had not realized before that Morse potentials had been used in the Bohr theory to explain the vibrational energy levels of diatomic molecules and the transition probabilities between different states. Hylleraas gives a very interesting discussion of the origin of wave mechanics. Harmonic oscillators, free rotators, and the hydrogen atom are considered in great detail, including transition coefficients. I particularly like the treatment of the Dirac equation and the relativistic hydrogen atom. The derivations and explanations are simple and convincing. Returning to the Schrödinger equation, Hylleraas has an excellent chapter on the perturbation of both degenerate and nondegenerate discrete states, with lots of problems and examples to illustrate the procedures. Of course, he uses the Hylleraas variational principle to solve for the first-order perturbation wave function! Among these examples are the perturbed simple harmonic oscillator, the $1/Z$ expansion of atoms (or ions) with a given number of electrons, and the Stark and Zeeman effects in atomic hydrogen. Periodic perturbations are considered from the standpoint of time-dependent forces. This leads to a good discussion of the absorption and emission of an atom in a radiation field (Einstein's A's and B's), refraction and dispersion, as well as the scattering of long-wave electromagnetic radiation. The next chapter is devoted to the helium atom considering various methods of approximation, reductions to three independent variables for S-states, and a discussion of the coordinate systems which Hylleraas has found useful in considering two-electron atoms. The remainder of the book is devoted to scattering problems: coherent and incoherent scattering of short-wave radiation, atomic form factors, sum rule for total scattering, scattering of electrons in a potential field, Rutherford's formula, the Born approximation, the perturbation series. The method of partial waves is then considered with considerable detail and illustrated by an excellent set of problems. The effect of electron exchange is considered for the scattering of fast electrons in a real atom. Electron scattering is then viewed in terms of a time-dependent perturbation. Next, the electromagnetic field corresponding to radiation is quantized. The interaction of this quantized field with atoms is considered. Finally, the quantum-electrodynamic method is used to develop the formula for the scattering of coherent and incoherent short-wave radiation.

This is truly a great book written by one of the greatest physicists of the twentieth century. Nowhere else will one find all of theoretical physics, presented in such a simple, elegant, rigorous fashion!

University of Wisconsin Theoretical Chemical Institute
Madison, Wisconsin
December 1969

JOSEPH O. HIRSCHFELDER

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PART III

Electromagnetism

Introduction

This Part follows the inductive method: Starting with simple basic laws like the Coulomb law, we gradually generalize such laws into the full set of Maxwell's electromagnetic equations. We have also followed the principle that mathematical deductions and considerations be sufficiently complete so that readers will not need to supplement their knowledge from other sources, except for some basic mathematical training.

The fairly broad discussion of electrostatics is justified by the similarity of electrostatic problems (potential theory, partial differential equations, boundary conditions, etc.) to a great variety of problems from other branches of theoretical physics.

In electromagnetism and electrodynamics, stress is laid upon the inner connection between different laws, which are sometimes presented as having a purely experimental basis, in the sense that there are clear interconnections through general principles, as for instance the principle of *actio* and *reactio*.

In the last section on electromagnetic radiation, or even in the previous paragraphs, the author would have preferred to use as the guiding principle the requirements of relativity theory, that electromagnetic equations be Lorentz-invariant. This procedure, was abandoned however, for practical reasons.

Our aim in Part III has been to contribute to the understanding of electromagnetism for those readers who have not had very extensive preliminary studies other than some experimental experience. In particular it has been prepared for students of theoretical physics and its many mathematical uses.

I am much indebted to my assistants Jan Trulsen and Kjell Aashamar for their devoted cooperation in preparing the manuscript.

CHAPTER 1

Electrostatics

1. NATURE OF ELECTRICITY

Positive and Negative Electric Charges

Electric phenomena undoubtedly have been observed by man from early time. We all know how easily audible, or even visible, small electric sparks can be produced by simply rubbing dry pieces of clothes together by chance. Particular substances were early known to produce electric phenomena easily. The ancient Greeks knew that amber was able to attract small and light bodies when rubbed by wool. The British physicist William Guilbert (1540–1603) showed that a number of substances had properties similar to amber; he termed them *electric* bodies after the Greek name *electron* for amber. Guilbert was an ingenious experimentator who made a number of other discoveries, among them his investigations of magnetic phenomena which became of great practical importance.

His countryman Steven Gray (1670–1736) discovered the fundamental difference between insulators and conductors, and the Frenchman Du Fay (1698–1739) explained the dual nature of electricity in form of two constituents, the glass and the resin electricity. He also realized the nature of electric forces: repulsive for the same kind and attractive for different kinds of electricity.

Our present names of "positive" and "negative" electricity relating to glass and resin we owe to the ingenious scientist Benjamin Franklin (1706–1790). These names are based on convention only, and we might perhaps have liked Franklin to have made the opposite choice. Today everyone knows that there is a real difference, that the electricity flowing in a metallic conductor is negative electricity in the form of free electrons, and that our first discovered and most prominent elementary particle is the *electron*. It is true that the discovery in 1932 of the positive electron, and later on the discovery of a multitude of particles and antiparticles, has made the nature of "negative" electricity more dubious.

Insulators and Conductors

If certain classes of bodies apparently cannot be electrified at all, the reason may well be that the electricity produced is moving away too rapidly to be detected. This is the case for bodies called *conductors*. Obviously they are capable of transporting electricity with a minimum of resistance through their interior or along their surface. Usually such bodies are metals but they may also be electrolytic solutions or ionized gases.

Bodies to which electric charges attach themselves fairly firmly and through which electricity is not discharged are called *insulators*. From our present knowledge of the constitution of matter the two states of material bodies are fairly well understood. In metals the carriers of electricity are the light and easily movable electrons in the form of free electrons: They are outer electrons from metallic atoms that have been loosened from their respective atoms as a result of the particular conditions for metallic bindings. In gases and electrolytes the carriers of electric charges are larger and heavier particles like charged atoms and molecules. They may have either positive or negative charges and are called *ions*.

In insulators no transport of electricity is possible because the electrons are firmly bound to their atoms or molecules. The binding forces are qualitatively of the electrostatic type mostly, originating from the heavily charged atomic nuclei. However, there are also particular forces that were not fully understood before the time of modern quantum mechanics. These forces are responsible for chemical bonds that may be characterized by the name of exchange forces and which were unknown before the time of wave mechanics. These forces are closely related to the formation of electron pairs on the basis of mutual orientation of eigenspins of the electrons. The firm binding of an electron, therefore, does not mean only a firm binding of an electron, but also a firm binding to the rest of electrons in the atom or molecule to which the electron belongs.

Electric Forces

It is easily demonstrated that the production of electric charges by rubbing processes simply consists of a separation of the two kinds of electricity. On rubbing a stick of glass or resin with a suitable cloth, no electric forces are observed because the stick is covered with cloth. Electric charges of opposite sign undoubtedly are attached to either of the bodies, however, which becomes evident when the cloth is removed and the charges are separated from each other.

Another way of separating electric charges is due to the phenomenon of *influence*. In that case the two kinds of electricity are drawn to either side of a metallic body by exterior electric forces. If one end of the body is touched by

hand or in some other way set in conductive connection with larger bodies, parts of the one kind of electricity may escape and leave the metallic body with a surplus of the opposite charge.

Such charges are easily detected by sensitive devices called *electroscopes* which owe their effects to forces between the electric charges. If suitably constructed and provided with measuring scales, they can be used for quantitative measurements; they are then called *electrometers.*

2. CONNECTIONS BETWEEN ELECTRIC CHARGES AND MECHANICAL FORCES. FIELDS AND POTENTIALS

The Law of Force

The most conspicuous property of electric charges is their mutual attraction or repulsion. For historical reasons this has become the basis of electric measurements and quantities; although other ways of creating suitable measuring units for electric phenomena have been tried, it cannot be denied that an elementary law of force is the simplest starting point and has the strongest power in the description of electric phenomena.

It is not difficult to fancy how electric charges may be divided into equal parts. Hence division of charges by powers of two is possible and may be used to isolate practically any fraction of a larger given quantity of charge. Conversely the adding up of any multiple of a smaller charge should not meet with any major difficulties. Hence we have different quantities of charge measured on some relative scale with which to work.

A realistic picture of an electric charge is a metallic sphere provided with a certain amount of electric charge. The smaller the sphere, the more suitable it becomes for accurately defined electric measurements. Such a sphere is sometimes called a test body. The name implies that the sphere should not only be small in size but also that its charge should be sufficiently small so as not to cause a sensible reaction on the distribution of the given charges that create the object of the measurements, namely, the *electric field.*

Let us stress the first property, the smallness of the sphere. At greater distances such a sphere may be thought of as something fairly equivalent to a mathematical point. Therefore, imagining the electric charges as placed on very minute metallic spheres, we arrive very close to the conception of point charges to which, for mathematical exactness, we want to refer our fundamental laws.

We now direct our attention to two such point charges of known relative magnitude as denoted by e_1 and e_2. Thinking in terms of small spheres with perfect isotropy, we shall omit any preference of direction. Given the coordinates of e_1, we find that it cannot matter whether e_2 is placed up or down or to the right or left. What matters is the magnitude of the charges and the

distance r between them. Axial symmetry with respect to their connecting line ensures that the direction of the force can be no other than along this line. The force is a genuine central force.

Moreover, if we place two charges e_2 and $-e_2$ side by side, the forces acting upon them from e_1 must be equal and opposite because if we unite the charges the force is zero. Hence the law of force must be

$$F = e_1 e_2 f(r) \tag{2.1}$$

with $f(r)$ an unknown function.

We have made F a single quantity. From Newton's principle of *actio* and *reactio* it follows that F represents twin forces: that from e_1 act on e_2 and the force of opposite direction that acts on e_1 from e_2.

Even though the function $f(r)$ is so far unknown we may dispose of its absolute magnitude by requiring that $f(1) = 1$. For equal charges $e_1 = e_2 = e$ at a unit distance we then have

$$F = e^2. \tag{2.2}$$

On measuring the mechanical force F the quantity of charge is known as measured in an absolute scale or expressed in absolute units. These are called electrostatic units; when the centimeter, gram, and second are used for fundamental units, the electrostatic units are said to belong to the CGS system.

If two charges are slowly changing their mutual distance r, the force between them is doing work. This may be expressed by saying that their mutual potential energy has changed. This change can be expressed by another function which may be termed the *potential function* and which is just the integrated force function

$$f(r) = -v'(r), \qquad v(r) = -\int_{\infty}^{r} f(r)\, dr. \tag{2.3}$$

On fixing the lower integral limit at infinity we have made a decision of only practical nature in requiring the, in principle arbitrary, zero level of the potential function to be at infinity. This is because the force function itself is assumed to be zero at infinite distances, so that for large distances the potential function approaches a constant value.

From (2.1) and (2.3) it now follows that

$$\int_{r}^{\infty} F(r)\, dr = e_1 e_2 v(r) = V(r). \tag{2.4}$$

Then $V(r)$ is the mutual potential energy of the two charges which equals the work done when the charges are separated to very large distances.

Electric Field Vector and Electrostatic Potential

We may now look upon the question in that way that e_2 is used as a test body placed in every conceivable position in the surroundings of e_1. The force on e_2 is measured, and if in particular we take $e_2 = 1$ the resulting field of force is called the electric vector field from e_1 which we denote by **E**. To deserve the characteristic of a test body e_2 should not be unity but rather extremely small. The formal value $e_2 = 1$ corresponds to measuring the field of force for a very small charge e_2 and then dividing by e_2 to obtain what above is termed the electric field.

It follows from the elementary law of force that we may write

$$\mathbf{E} = ef(r)\hat{\mathbf{r}} = -e\nabla v(r) \tag{2.5}$$

with $\hat{\mathbf{r}} = \mathbf{r}/r$ the unit vector in direction from the charge e to the field point **r**. More simply we write

$$\mathbf{E} = -\nabla\Phi \tag{2.6}$$

with

$$\Phi = ev(r). \tag{2.6a}$$

Again let e_k, $k = 1, 2, \cdots$, be a number of charges placed at different points in space. It is easily found that the electric vector field produced jointly by all of them can be written in the form (2.6) with

$$\Phi = \sum_k e_k v(r_k) \tag{2.6b}$$

and with r_k the distances from the individual charges e_k.

The function Φ is called the electrostatic potential or briefly the potential of the electrostatic field **E**. If the field is considered known, the potential can be expressed by the equation

$$\Phi = \int_{\mathbf{r}}^{\infty} \mathbf{E}\, d\mathbf{r} \tag{2.6c}$$

whereby the path of integration from an infinitely distant point to the field point in question is immaterial. This follows from the definite value of Φ in (2.6*b*) as based upon the conception of an elementary central force. Adopting the principle that no work can be gained by letting an electric charge move around a closed path, we obtain the same result.

The advantage of using the potential of the field as given by a single function rather than the three-dimensional quantity, the field vector **E**, will soon be obvious.

The Potential of a Charged Sphere and the Coulomb Law

Let **r** be the vector from the center O of a sphere of radius a to an arbitrary field point P (outside) or P' (inside the sphere). Let r' be the distance PQ to a

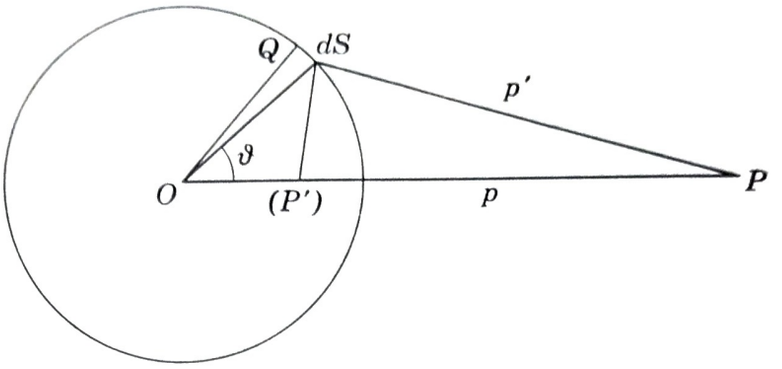

Fig. 1-1. Potential of a charged sphere surface.

source point Q on the sphere or rather the surface element

$$dS = a^2 \sin \vartheta \, d\vartheta \, d\varphi \tag{2.7}$$

at this point. If e is the total charge on the sphere the charge density is

$$\sigma = \frac{e}{4\pi a^2} \tag{2.7a}$$

and the potential at P becomes

$$\Phi = \int \sigma \varphi(r') \, dS = \frac{e}{2} \int_0^\pi \varphi(r') \sin \vartheta \, d\vartheta \tag{2.7b}$$

on integrating over the equatorial angle φ.

Next observing that

$$r'^2 = r^2 + a^2 - 2ra \cos \vartheta,$$
$$r' \, dr' = ra \sin \vartheta \, d\vartheta, \tag{2.7c}$$

and putting

$$r\varphi(r) = G'(r), \tag{2.7d}$$

we obtain

$$\Phi(r) = \frac{e}{2\pi a} \int_{r-a}^{r+a} G'(r') \, dr' = \frac{e}{2\pi a} [G(r + a) - G(|r - a|)]. \tag{2.8}$$

Hence there are different expressions for the potential outside and inside the sphere, $r \gtrless a$. If the Coulomb law is adopted, we have

$$f(r) = \frac{1}{r^2}, \qquad \varphi(r) = \frac{1}{r}, \qquad G(r) = r + c, \tag{2.8a}$$

and the result is

$$\Phi(r) = \frac{e}{r}, \qquad r > a, \tag{2.9}$$

$$\Phi(r) = \frac{e}{a}, \qquad r < a. \tag{2.9a}$$

This means that the potential is constant and that there is no field of force inside the sphere. Obviously this result is not obtainable on any other basis than the Coulomb law.

Now assume that the basic law of force were different: The potential inside a metallic sphere with even surface distribution of charge would no longer be constant. In order to restore constancy of the potential and absence of an electric field inside the sphere a spatial spherically symmetric charge distribution $\rho(r)$ would be needed. The analytic form of the distribution corresponding to an arbitrary law of force is not explicitly obtainable except maybe in approximate form for slight deviations of the force function $f(r)$ from the Coulomb law, say $f(r) = 1/r^{2+\varepsilon}$.

Any further discussion of details is, however, of minor interest because the results obtained are against all experience. When two concentric spherical surfaces in metallic connection establish electrostatic equilibrium, the outer one will take all the charge. On removing the outer sphere there will be no charge left. This is the basis for the famous experiments of Cavendish in 1773 which, as proved by later analysis, ensures the deviation from the Coulomb law to be smaller than $|\varepsilon| = \frac{1}{50}$ in the above, more general, law. This is far beyond the accuracy that could be obtained by Coulomb himself in later experiments by direct measurements of forces between electric charges. A hundred years later Maxwell was able to conceive experiments, on the same principal basis as those of Cavendish, which led to a verification of the Coulomb law within the narrow limits of $|\varepsilon| < 1/21{,}600$.

3. THE GAUSS THEOREM AND THE POISSON EQUATION

The Field Flux from a Point Charge

Consider a single point charge e inside or outside a given closed surface. Let the surface elements be represented by vectors $d\mathbf{S}$ normal to the surface in outward direction and equal in length to the area of the surface element as measured in units of area. The integral

$$N = \int \mathbf{E}\, d\mathbf{S} \tag{3.1}$$

is called the flux of $\mathbf{E}$ through the closed surface. Adopting the Coulomb law for $\mathbf{E}$, we see by very simple geometrical considerations that the flux of the field from a charge e is one and the same, namely $N = 4\pi e$ for any position of e inside the surface, and hence also independent of the shape and extension of the surface. Only if e is outside the surface is the result different, namely, $N = 0$. This is sometimes called the Gauss law of electrostatics, to be distinguished from his famous integral theorem to which the law is intimately related.

The result also applies to any number of charges inside a closed surface and hence can be expressed by the equation

$$\int \mathbf{E}\, d\mathbf{S} = 4\pi \sum_k e_k. \tag{3.1a}$$

Assuming a continuous distribution ρ of electric charges, we are forced by intuitive reasoning to accept the corresponding law

$$\int \mathbf{E}\, d\mathbf{S} = 4\pi \int \rho\, d\tau. \tag{3.1b}$$

Now the flux of a vector through an infinitely small closed surface around a point in space gives rise to the definition of a scalar derivative of the field called its *divergence*. The definition is equivalent with the general validity of the Gauss integral theorem

$$\int \mathbf{E}\, dS = \int \operatorname{div} \mathbf{E}\, d\tau. \tag{3.2}$$

If we apply the theorem to an infinitely small cube of side lengths dx, dy, dz, the result is seen to be

$$\operatorname{div} \mathbf{E} = \nabla \mathbf{E} = \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{dz}, \tag{3.2a}$$

as expressed in Cartesian coordinates. The expression is easily found to be invariant against rotations of the coordinate system.

We are now able to express the fundamental law of electrostatics as a differential law, that is, in the form of a differential equation, at least for continuous distribution of electric charges. The point charges present some difficulties in introducing singularities in the field. The difficulty can be formally removed by introducing certain improper functions known under the name of Dirac delta functions. We therefore venture to write

$$\operatorname{div} \mathbf{E} = 4\pi\rho + 4\pi \sum_k e_k\, \delta(\mathbf{r} - \mathbf{r}_k). \tag{3.3}$$

Here $\delta(\mathbf{r} - \mathbf{r}_k)$ is a delta function with properties roughly described as follows. Its value when $\mathbf{r} \neq \mathbf{r}_k$ is zero. When $\mathbf{r} = \mathbf{r}_k$ it has an infinite positive value. Its volume integral across the singular point $\mathbf{r} = \mathbf{r}_k$ shall, however, exist and have the value 1,

$$\int \delta(\mathbf{r} - \mathbf{r}_k)\, d\tau = 1. \tag{3.3a}$$

It follows that a volume integral of the following form comprising the singular

point has the value

$$\int F(\mathbf{r}')\,\delta(\mathbf{r}' - \mathbf{r}_k)\,d\tau' = F(\mathbf{r}_k). \tag{3.3b}$$

A delta function of several variables can be expressed in a number of ways by one-dimensional delta functions. We may write

$$\delta(\mathbf{r}) = \delta(x)\,\delta(y)\,\delta(z), \tag{3.3c}$$

where $\delta(x)$ and so forth, are elementary Dirac delta functions. If polar coordinates r, ϑ, φ are used the product function would look quite different.

We are returning to the use of delta functions in the sequel for the purpose of easier determination of so-called Green's functions.

The Coulomb Potential of a Continuous Charge Distribution

The Coulomb potential of a point charge distribution is

$$\Phi = \sum_k \frac{e_k}{r_k}. \tag{3.4}$$

It is consistent with the expression

$$\Phi = \int \frac{\rho}{r}\,d\tau \tag{3.4a}$$

if the point charge distribution is written formally as

$$\rho = \sum_k e_k\,\delta(\mathbf{r} - \mathbf{r}_k). \tag{3.5}$$

This is nothing more than to imagine the charges e_k as being of a very minute extension rather than geometrical points. It is obvious that if (3.4) is true, there is no other possible expression for the potential of a continuous charge distribution than that of (3.4*a*).

Nevertheless we shall deduce the result (3.4*a*) from the differential equation (3.3) by a particular method, called Green's method. The aim is to demonstrate the method rather than to confirm the above obvious results. It may also give us the opportunity to state that the distances in (3.4) and (3.4*a*) are taken in the sense of

$$\begin{aligned} r_k &= |\mathbf{r}_k|, \qquad \mathbf{r}_k = \mathbf{r}_p - \mathbf{r}_q, \\ r &= |r|, \qquad \mathbf{r} = \mathbf{r}_p - r_q, \end{aligned} \tag{3.6}$$

with $\mathbf{r}_p$ and $\mathbf{r}_q$ the position vectors of the field point P and the source point Q, respectively, as referred to an arbitrary origin of the coordinate system. The $\mathbf{r}_q$ then refers always to a point charge e_k or to the volume element $d\tau$ (or $d\tau_q$) with the charge density $\rho(\mathbf{r}_q)$.

We now write

$$\mathbf{E} = -\nabla\Phi, \tag{3.7}$$

which is the general relation between the electrostatic field and the potential, and obtain by (3.3) the Poisson equation for continuous charge distribution

$$\nabla^2\Phi = -4\pi\rho. \tag{3.8}$$

Here we apply the Green's function

$$\psi = \frac{1}{r}, \qquad \nabla^2\psi = 0. \tag{3.8a}$$

On combining the above equations we first obtain

$$\frac{1}{4\pi}\,\mathrm{div}\,(\Phi\nabla\psi - \psi\nabla\Phi) = \rho\psi. \tag{3.8b}$$

In this equation we may consider Φ, ρ, and ψ functions of the source point coordinates $\mathbf{r}_q$ with the differential operator ∇ referring to the same coordinates as well. The field point P is provisionally considered a fixed point which we exclude from the domain of integration by a small sphere.

On multiplying by the volume element $d\tau$ at Q and integrating, the left-hand side integral can be transformed into two surface integrals, the first one taken over a distant surface and neglected as approaching zero. The second integral is taken over a minute sphere of radius a and a total surface area $4\pi a^2$ around the field point P.

It is obvious that as $a \to 0$ the second left-hand term of (3.8*b*) gives a zero contribution. In the first term Φ approaches the value sought for, namely $\Phi(\mathbf{r}_p)$, which is independent of $\mathbf{r}_q$ and hence can be taken outside the integral. Inside the integral there remains only

$$\frac{1}{4\pi}\nabla\psi = -\frac{\hat{\mathbf{r}}}{4\pi r^2}, \tag{3.8c}$$

with $\hat{\mathbf{r}}$ the unit vector pointing from P to Q. The outer normal to the surface as reckoned from the domain of integration in space, however, will be the inner normal of the sphere. Hence, with $\mathbf{n} = -\hat{\mathbf{r}}$

$$\frac{\mathbf{n}}{4\pi}\nabla\psi = \frac{1}{4\pi r^2} = \frac{1}{4\pi a^2}. \tag{3.9}$$

Applying the Gauss theorem, we find that the surface integration now consists simply in multiplying (3.9) by the surface area $4\pi a^2$, which gives unity. On the left-hand side of (3.8*b*) there remains, however, the unknown potential $\Phi(\mathbf{r}_p)$ in the field point P which now becomes the left-hand side of the

total integral. On introducing $\psi = 1/r$ the right-hand side is simple, and the result is

$$\Phi(\mathbf{r}_p) = \int \frac{\rho(\mathbf{r}_q)}{r}\, d\tau. \tag{3.10}$$

4. DISCONTINUOUS FIELDS

Surface Layers

A continuous charge distribution produces a continuous electric field. The only sort of discontinuous fields so far encountered are those of a point charge and the charged surface of a sphere. In the latter case the surface density and the discontinuity of the normal component of the field vector were

$$\sigma = \frac{e}{4\pi a^2}, \qquad E_n = \Delta E_n = \frac{e}{a^2}. \tag{4.1}$$

Hence

$$\Delta E_n = 4\pi\sigma \tag{4.2}$$

which is a general result irrespective of the geometrical form of the surface or possible variations of the surface charge. Moreover, the tangential component has no discontinuity.

To see this consider an infinitesimal region of a charged surface of continuously variable density. Whatever may be the variation of charge density, it may be treated as constant in an infinitesimal region. Similarly the electric fields on either side of the surface may be treated as constant fields. Because of the gradient character of the field, namely, $E = -\nabla\Phi$ we have

$$\text{curl } \mathbf{E} = 0, \tag{4.3}$$

from which on the basis of the Stokes' theorem we obtain the zero integral

$$\oint \mathbf{E}\, d\mathbf{s} = 0 \tag{4.3a}$$

along any closed curve of vectorial line element $d\mathbf{s}$.

For this curve we choose the rectangle *cdef* with the parallel sides *cd* and *ef* on either side of the surface as indicated by the line *ab* and with the perpendicular sides *de*, *cf* taken negligibly small in comparison to *cd*, *ef*. It follows immediately from (4.3*a*) that the tangential component E_t goes continuously through the surface layer. In particular, for a conductor, the outside field is perpendicular to the surface and the inside field zero. Hence the tangential component is zero on either side. In insulators it may be different.

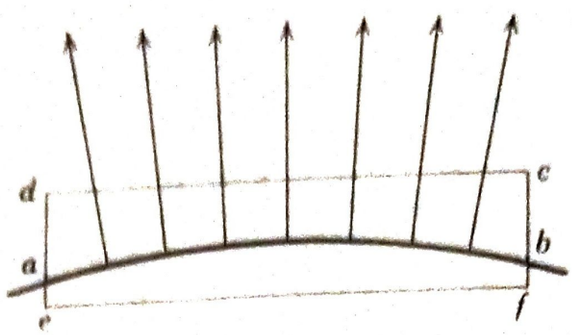

Fig. 1-2. Field discontinuity of a charged surface.

As to the normal component we may use the same figure imagining $cdef$ to be a flattened pillbox of basic area dS, hence enclosing the charge σdS. Let $\mathbf{n}$ be the surface normal to, say, the upper side, the total flux through the closed pillar box surface being $\Delta E_n\, dS$. Hence (4.2) for the charged metallic sphere is true for any charged surface. (See Fig. 1-2.)

The Charged Rod

Even though a charged line is a rather artificial construction, it deserves some attention because of its connection with elliptic coordinates. Consider a rod of length $2c$ with an infinitesimal cross section and with a charge density per unit length $e/2c$.

If the z-axis is taken along the line with its origin in the center of the rod, we have

$$\Phi = \frac{e}{2c}\int_{-c}^{c} \frac{d\zeta}{(x^2 + y^2 + (z-\zeta)^2)^{1/2}}. \tag{4.4}$$

Elementary integration gives

$$\Phi = \frac{e}{2c}\log\frac{c - z + R_+}{-c - z + R_-}. \tag{4.4a}$$

Here

$$\left.\begin{matrix} R_+ \\ R_- \end{matrix}\right\} = (x^2 + y^2 + (z \mp c)^2)^{1/2} \tag{4.4b}$$

are the distances to the field point (x, y, z) from the right and left ends of the rod, respectively.

The formula becomes somewhat simplified if elliptic coordinates ξ, η, ζ are introduced by the equations

$$R_+ = c(\xi - \eta), \qquad R_- = c(\xi + \eta), \qquad \frac{y}{x} = \tan\varphi. \tag{4.5}$$

If written the other way as

$$\xi = \frac{1}{2c}(R_+ + R_-), \qquad \eta = \frac{1}{2c}(-R_+ + R_-), \tag{4.5a}$$

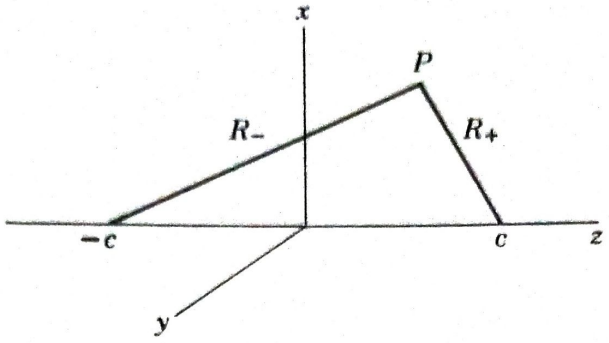

Fig. 1-3. The potential of a charged rod.

the coordinate surfaces $\xi = \text{const}$ and $\eta = \text{const}$ are seen to be confocal rotational ellipsoids and hyperboloids, respectively, whereas $\varphi = \text{const}$ are planes through the rotational symmetry axis.

The forms (4.5) and (4.5*a*) of the coordinate transformations may serve well for many purposes. It is customary, however, and usually more expedient to have them expressed in Cartesian coordinates;

$$\begin{aligned} x &= c\sqrt{(\xi^2 - 1)(1 - \eta^2)}\cos\varphi, \\ y &= c\sqrt{(\xi^2 - 1)(1 - \eta^2)}\sin\varphi, \\ z &= c\xi\eta. \end{aligned} \tag{4.6}$$

then ξ, η, φ are called *prolate* elliptic coordinates with rotational symmetry. In these coordinates the potential (4.4*a*) becomes

$$\Phi = \frac{1}{2c}\log\frac{1 - \xi\eta + \xi - \eta}{-1 - \xi\eta + \xi + \eta} = \frac{1}{2c}\log\frac{\xi + 1}{\xi - 1}, \tag{4.7}$$

and this proves that the prolate rotational ellipsoids of $\xi = \text{const}$ are surfaces of constant potential. The confocal rotational hyperboloids in their intersections with planes through the rotational axis then represent electric vector lines orthogonal to the potential surfaces.

To master the geometry of the field we write down the square line element

$$\begin{aligned} ds^2 &= dx^2 + dy^2 + dz^2 \\ &= c^2\left[\frac{\xi^2 - \eta^2}{\xi^2 - 1}\,d\xi^2 + \frac{\xi^2 - \eta^2}{1 - \eta^2}\,d\eta^2 + (\xi^2 - 1)(1 - \eta^2)\,d\varphi^2\right]. \end{aligned} \tag{4.8}$$

From this expression we easily find the line elements corresponding to variations of either of the elliptic coordinates:

$$\frac{\partial s}{\partial \xi} = c\left(\frac{\xi^2 - \eta^2}{\xi^2 - 1}\right)^{1/2}, \quad \frac{\partial s}{\partial \eta} = c\left(\frac{\xi^2 - \eta^2}{1 - \eta^2}\right)^{1/2}, \quad \frac{\partial s}{\partial \varphi} = c[(\xi^2 - 1)(1 - \eta^2)]^{1/2}. \tag{4.8a}$$

This among others gives the volume element

$$d\tau = c^3(\xi^2 - \eta^2)\, d\xi\, d\eta\, d\varphi \tag{4.8b}$$

and the square gradient

$$(\nabla\Phi)^2 = \frac{1}{c^2(\xi^2 - \eta^2)}\left[(\xi^2 - 1)\left(\frac{\partial\Phi}{\partial\xi}\right)^2 + (1 - \eta^2)\left(\frac{\partial\Phi}{\partial\eta}\right)^2 + \frac{\xi^2 - \eta^2}{(\xi^2 - 1)(1 - \eta^2)}\left(\frac{\partial\Phi}{\partial\varphi}\right)^2\right] \tag{4.8c}$$

from which in the usual way one obtains

$$\nabla^2 = \frac{1}{c^2(\xi^2 - \eta^2)}\left[\frac{\partial}{\partial\xi}(\xi^2 - 1)\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}(1 - \eta^2)\frac{\partial}{\partial\eta} + \left(\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2}\right)\frac{\partial^2}{\partial\varphi^2}\right]. \tag{4.8d}$$

Denoting by $\mathbf{n}$ the normal to the potential surfaces, and hence the unit vector along the vector lines $\eta = \text{const}$, $\varphi = \text{const}$, the field is given by

$$\mathbf{E} = -\frac{\partial\Phi}{\partial\xi}\nabla\xi = \frac{e}{c}\frac{1}{\xi^2 - 1}\cdot\frac{\mathbf{n}}{c}\left(\frac{\xi^2 - 1}{\xi^2 - \eta^2}\right)^{1/2}. \tag{4.9}$$

On the other hand, the surface element is easily seen from (4.8*a*) to be

$$d\mathbf{S} = c^2\mathbf{n}[(\xi^2 - \eta^2)(\xi^2 - 1)]^{1/2}\, d\eta\, d\varphi. \tag{4.9a}$$

Therefore

$$\mathbf{E}\, d\mathbf{S} = e\, d\eta\, d\varphi \tag{4.9b}$$

and the flux between two consecutive hyperboloids of distance $d\eta$ becomes $2\pi e\, d\eta$. Integrating from $\eta = -1$ to $\eta = 1$, we obtain the result $4\pi e$ corresponding to the Gauss law.

Along the rod the line element is $c\, d\eta$. From the flux $2\pi e\, d\eta$ we see that the charge on that element of the rod is $\frac{1}{2}e\, d\eta$. Hence the line charge density is

$$\lambda = \frac{e}{2c}, \tag{4.9c}$$

as it was supposed to be. (See Fig. 1-4.)

The Electric Dipole

Consider two electric charges e and e' placed at a certain distance; it appears that the resulting problem must be simpler than that of the charged rod. In fact it is not, even though the potential can easily be set up and the field evaluated.

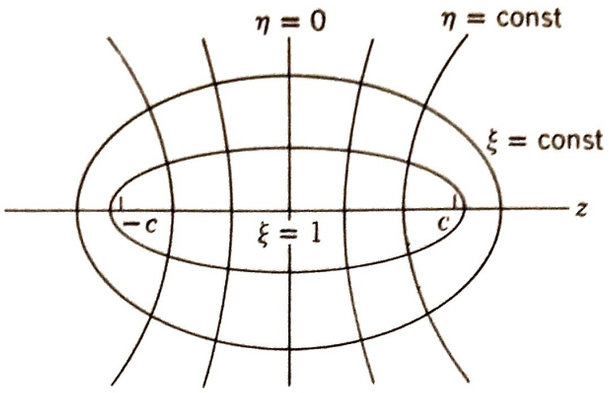

Fig. 1-4. Potential surfaces and electric vector lines of a charged rod.

This is true even if we take the charges of equal size and opposite sign to constitute a physical electric dipole. The equation for equipotential surfaces is easily found to be

$$e\left(\frac{1}{r} - \frac{1}{r'}\right) = \text{const.} \tag{4.9d}$$

The surfaces are hyperboloid-like surfaces; however, considerably more complex analytically than the rotational hyperboloids of the charged rod. We therefore turn to the simpler field of a mathematical dipole with two infinitely large electric charges $\pm e$ at an infinitely short distance a, so that $p = ea$, the electric dipole moment, stays finite.

Put $-e$ at the origin and e on the z-axis at $z = a$; then the potential at P is

$$\Phi = \frac{e}{r'} - \frac{e}{r} = \frac{e(r - r')}{rr'} \tag{4.10}$$

To the first approximation

$$r - r' = a \cos \vartheta = \frac{\mathbf{ar}}{r}. \tag{4.10a}$$

Hence, with $e\mathbf{a} = \mathbf{p}$ and putting $r' = r$ in the denominator,

$$\Phi = \frac{\mathbf{pr}}{r^3}. \tag{4.10b}$$

The field vector $\mathbf{E} = -\nabla\Phi$ becomes

$$\mathbf{E} = \frac{-\mathbf{p} + 3(\mathbf{p}\hat{\mathbf{r}})\hat{\mathbf{r}}}{r^3} \tag{4.10c}$$

with $\hat{\mathbf{r}}$ the unit vector in direction of $\mathbf{r}$. The field corresponds to the magnetic field of an elementary magnet. In the so-called Gauss main positions at the same distances on either side along the axis and at any point at the same

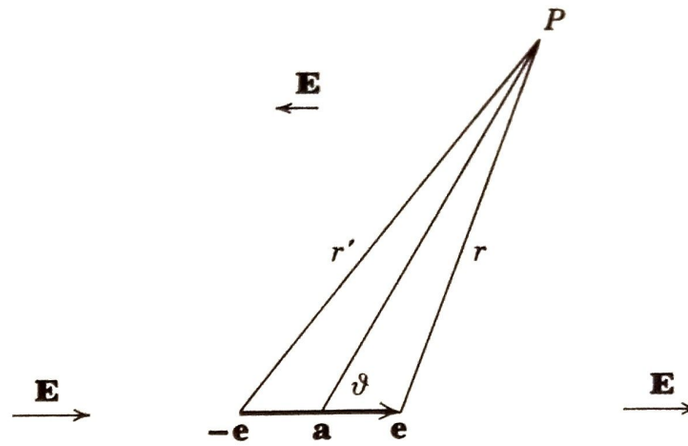

Fig. 1-5. Electric dipole. **E** = electric field vectors in main Gauss' positions.

distance perpendicular to the axis, the ratio of the field strengths is 2:1, the fields, however, having opposite directions. (See Fig. 1-5.)

Electric Multipoles

The source of the potential and the field in (4.10*b*) and (4.10*c*) may be characterized as a genuine mathematical dipole. A real dipole produced by two separate charges as in (4.10) is a superposition of entities called *multipoles*. (See Figs. 1-6 and 1-7.) An expansion of $1/r'$ in (4.10) in terms of reciprocal powers of r would read

$$\Phi = \sum_{n=1}^{\infty} \frac{ea^n}{r^{n+1}} P_n(\cos\vartheta), \qquad \cos\vartheta = \frac{z}{r}. \tag{4.11}$$

With x, y, z the coordinates of the field point P the functions $P_n(\cos\vartheta)$ are ordinary Legendre polynomials. The coefficients ea^n of the expansion are called multipole momenta. For small a and large n they are extremely small but finite for finite a. The multipoles themselves are called quadrupoles,

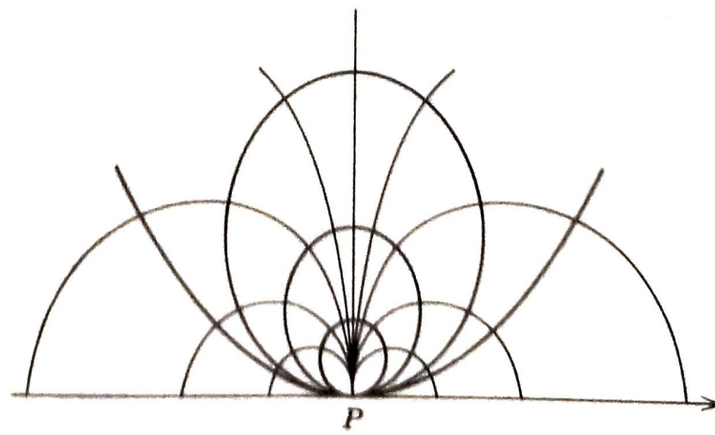

Fig. 1-6. Electric field lines and potential surfaces of a dipole.

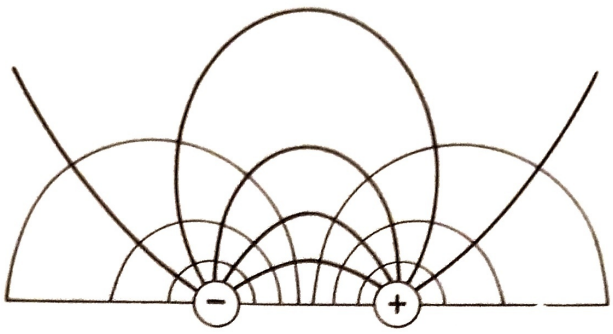

Fig. 1-7. Electric field lines and potential surfaces of separated equal charge of opposite sign.

sextopoles, octopoles, and so on, for $n = 2, 3, 4, \cdots$. (For an illustration of multipoles see Fig. 1-8.)

For the Legendre polynomials we have the definition from potential theory

$$\frac{1}{(1 - 2s\xi + s^2)} = \sum_n s^n P_n(\xi), \qquad |s| < 1. \tag{4.12}$$

Another definition might be derived by comparing the expressions (4.10) and (4.11). Put

$$r' = [x^2 + y^2 + (z - a)^2]^{1/2} \tag{4.13}$$

and expand $1/r'$ in powers of a by means of the Taylor series

$$\frac{1}{r'} = \sum_{n=0}^{\infty} \frac{a^n}{n!} \left(\frac{d^n}{da^n} \frac{1}{r'}\right)_{a=0} = \sum_{n=0}^{\infty} \frac{a^n}{n!} (-1)^n \frac{d^n}{dz^n} \frac{1}{r}. \tag{4.13a}$$

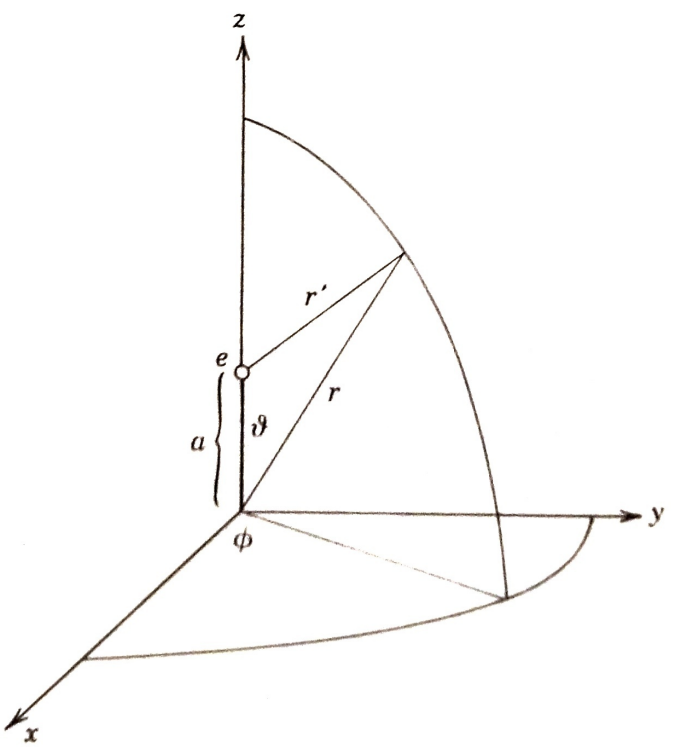

Fig. 1-8. Multipoles.

Hence

$$P_n\left(\frac{z}{r}\right) = \frac{(-1)^n r^{n+1}}{n!}\frac{d^n}{dz^n}\frac{1}{r}, \tag{4.13b}$$

which gives

$$P_0\left(\frac{z}{r}\right) = 1, \qquad P_1\left(\frac{z}{r}\right) = \frac{z}{r}, \qquad P_2\left(\frac{z}{r}\right) = \frac{1}{2}\left[3\left(\frac{z}{r}\right)^2 - 1\right], \qquad \text{etc.} \tag{4.13c}$$

Electric Dipole Layers

Consider two electric layers of surface charge density σ and $-\sigma$ at a mutual distance a. It may be called a dipole layer of strength

$$p = \sigma a \tag{4.14}$$

or of vectorial dipole density

$$\mathbf{p} = \sigma \mathbf{a} \tag{4.14a}$$

with $\mathbf{p}$ in the normal direction to the dipole layer. The layer need not be plane, and even σ and a may vary provided that their product p is constant. The possibility of a variable dipole density we shall disregard.

For the double layer of a plate condenser the field between the plates is not strictly homogeneous, and even deviates considerably at the edges of the condenser. To study the deviation we consider the electric field produced by a single surface element of charge density σ, in particular its component normal to the surface element. (See Fig. 1-9.) Let ϑ be the angle between the surface normal and the direction to the field point; at a distance r the normal component of the field is

$$E_n = \cos\vartheta \frac{\sigma\, dS}{r^2} = \sigma\, d\Omega, \tag{4.15}$$

where $d\Omega$ is the solid angle of $d\mathbf{S}$ as seen from the field point. A similar expression is obtained for a surface element of negative charge to be thought of as being above the point P as indicated in Fig. 1-10.

The above result provides a simple way of studying the normal component of the electric field of a plate condenser. At large dimensions of the plates and with a narrow gap the plates are seen under a solid angle of practically 4π. The deviation may be described by the solid angle under which the opening between the plates is seen. At the edges of the plates this angle is at

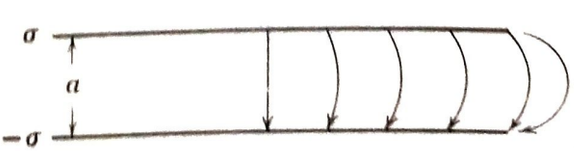

Fig. 1-9. Field deviation in a plate condenser.

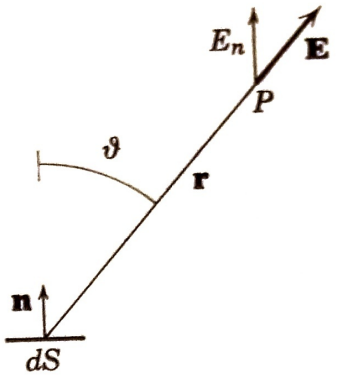

Fig. 1-10. The electric field of a charged surface element.

least 2π. Hence at the edges the normal component E_n is at least less than one half of its value in the central part of the condenser.

The reasoning, of course, applies only to condenser plates with presumed constant surface density. The deviation of this density from its value in the central region of the plates must be studied simultaneously with the deformation of the field; this can be done correctly only by solving the Laplace equations for the field with appropriate boundary conditions.

The Potential of a Dipole Layer

We now return to the genuine dipole layer, that is, one of very small thickness in comparison with its extension and with a constant dipole density. The layer need not be plane but may have any curvature. We consider, however, a layer of finite extension with a well-defined boundary curve. Its positive side is defined by the dipole direction.

Consider now an area element dS and the vector $\mathbf{r}$ to a field point P. The potential becomes

$$\Phi = \int \frac{\mathbf{pr}}{r^3}\, dS. \tag{4.16}$$

Now

$$\mathbf{pr} = pr\cos\vartheta, \tag{4.16a}$$

where $\cos\vartheta = \hat{\mathbf{p}}\hat{\mathbf{r}}$ is the projection of the surface normal on the unit vector $\hat{\mathbf{r}}$, and $dS\cos\vartheta/r^2$ is the projection of the surface element dS on the unit sphere around p. If this solid angle is called $d\omega$, the potential becomes

$$\Phi = p\omega, \tag{4.17}$$

where ω is the solid angle subtended by the positive side of the layer as viewed from P. See Fig. 1-11.

The potential has a discontinuity in the layer. When the field point passes from the positive to the negative side of the layer, the solid angle is counted negative. If the layer is flat, we have simply the potentials $2\pi p$ and $-2\pi p$ on

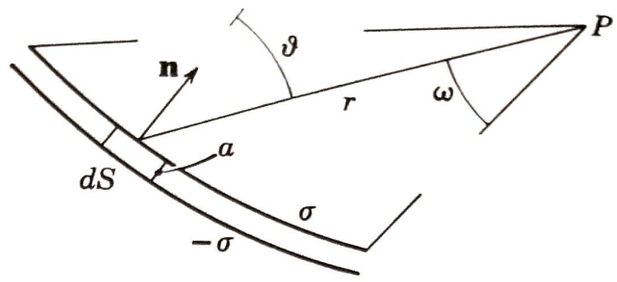

Fig. 1-11. Potential $a\sigma\omega$ of a dipole layer.

either side with a discontinuity of

$$4\pi p = 4\pi\sigma a, \tag{4.18}$$

as it must be, owing to the opposite direction of the electric field strength $E = 4\pi\sigma$ between the two single layers of charge density $\pm\sigma$ at a distance a.

If the layer is curved, it is the position of the boundary curve that determines the two potentials. If the double layer is a half-sphere with its positive side pointing outward, the potentials at the middle point of the surfaces are

$$\Phi_+ = \sqrt{2}\,\pi p, \qquad \Phi_- = (4 - \sqrt{2})\pi p. \tag{4.18a}$$

5. SOLUTIONS OF THE LAPLACE AND POISSON EQUATIONS

Uniqueness of the Solution of Laplace's Equation in a Bounded Region

In charge-free space the differential equation for the electrostatic potential is the Laplace equation

$$\nabla^2\Phi = 0. \tag{5.1}$$

With the restriction that the potential be zero at infinity the only possible type of solution is that of the Coulomb potentials e_k/r_k, that is, potentials with given singularities corresponding to point charges. An infinity of variations of the solution can be found by adding Coulomb potentials of that kind. The only way of making the solution of the Laplace equation unique is to state that no such singularities exist apart from a certain number of points. If these points are excluded from the region of integration by closed surfaces with appropriate boundary conditions on the surfaces, the uniqueness of the solution is guaranteed.

Similarly, if we look for a solution of the Laplace equation in a finite and bounded region in space, uniqueness is obtained by requiring appropriate boundary conditions for the solution.

The nature of the conditions is most easily found from the differential equation itself. Let

$$\Phi' = \Phi_1 - \Phi_2 \tag{5.2}$$

be the difference of two possibly different solutions, we have

$$\nabla^2\Phi' = 0 \tag{5.2a}$$

and also

$$\operatorname{div}(\Phi' \nabla\Phi') = (\nabla\Phi')^2 \tag{5.2b}$$

because of (5.2*a*). Integrating over the bounded region, on transforming the left-hand side integral into a surface integral on the boundary by the Gauss theorem, we find

$$\int (V\Phi')^2 \, d\tau = \int \Phi' \frac{\partial\Phi'}{\partial n} \, dS. \tag{5.3}$$

If on the surface $\Phi' = 0$, which will be the case if Φ_1 and Φ_2 satisfy the same boundary condition for the potential Φ, both integrals are zero and

$$\nabla\Phi' = 0, \qquad \Phi' = 0. \tag{5.3a}$$

The result is not only $\nabla\Phi_1 = \nabla\Phi_2$ but even $\Phi_1 = \Phi_2$.

If, on the other hand, the normal derivative $\partial\Phi/\partial n$ is required to be unique on the boundary, hence $\partial\Phi'/\partial n = 0$, the integrals (5.3) are again zero with the result that $\nabla\Phi_1 = \nabla\Phi_2$; however, $\Phi_1 - \Phi_2 = \text{const}$.

The first condition, of given Φ at the boundary, is called the Dirichlet condition. The second, of given $\partial\Phi/\partial n$, is the Neumann condition; when both quantities are required to be given simultaneously, it is called the Cauchy condition.

Obviously the Cauchy condition cannot be satisfied owing to the properties of the differential equation.

Solution of Poisson's Equation in a Bounded Area

With given continuous charge density $\rho(\mathbf{r})$ in unlimited space, the Poisson equation being

$$\nabla^2\Phi = -4\pi\rho, \tag{5.4}$$

we find by generalization of point charge potentials that

$$\Phi(\mathbf{R}) = \int \frac{\rho(\mathbf{R}')}{r} \, d\tau, \qquad r = |\mathbf{r}|, \qquad \mathbf{r} = \mathbf{R} - \mathbf{R}'. \tag{5.4a}$$

Here for greater clarity we have denoted field and source point by the space vectors $\mathbf{R}$ and $\mathbf{R}'$, respectively, in an arbitrary coordinate system, leaving as usual r and $\mathbf{r}$ for the mutual distance.

We now divide the infinite space into two parts: an inner one C bounded by a closed surface G and the outside region C'. From the equations

$$\rho(\mathbf{R}') = -\frac{1}{4\pi} \nabla'^2\Phi(\mathbf{R}'), \qquad \nabla'^2 \frac{1}{r} = 0, \tag{5.4b}$$

we then obtain the relation

$$\frac{\rho(\mathbf{R}')}{r} = \frac{1}{4\pi}\,\mathrm{div}'\left(\Phi\nabla'\frac{1}{r} - \frac{1}{r}\nabla'\Phi\right). \tag{5.5}$$

We now integrate over the outside region, using the Gauss theorem to transform the right-hand side into a surface integral

$$\int_{C'}\frac{\rho(\mathbf{R}')}{r}\,d\tau = \frac{1}{4\pi}\int_G\left(\Phi\frac{\mathbf{nr}}{r^3} - \frac{\mathbf{n}\nabla'\Phi}{r}\right)dS. \tag{5.5a}$$

Here $\mathbf{n}$ is the inside normal of the surface G and the sign of the first term of the integrand comes from the definition of $\mathbf{r}$ in (5.4*a*). The first term corresponds to a dipole density

$$\mathbf{p} = \frac{1}{4\pi}\Phi\mathbf{n} \tag{5.5b}$$

on the surface which may be thought of as a discontinuity of the potential from $\Phi = 0$ outside to $\Phi = 4\pi p$ inside the boundary. Moreover we may write

$$-\mathbf{n}\nabla'\Phi = E_n = 4\pi\sigma. \tag{5.5c}$$

Adding also the inside integral from (5.4*a*), we obtain the result

$$\Phi(\mathbf{R}) = \int_C\frac{\rho(\mathbf{R}')}{r}\,d\tau + \int_G\left(\frac{\mathbf{pr}}{r^3} + \frac{\sigma}{r}\right)dS. \tag{5.6}$$

The solution is illustrated in Fig. 1-12.

The surface integrals are then Coulomb potentials of fictitious surface charges and double layers on the boundary equivalent to an unknown possible outside charge distribution.

Green's Function in Electrostatics

The so-called Green's method for solving inhomogeneous differential equations is well-known and has a much wider application than that used here in electrostatics. The basic element of the method is the Green function which is a particular solution of the corresponding homogeneous equation.

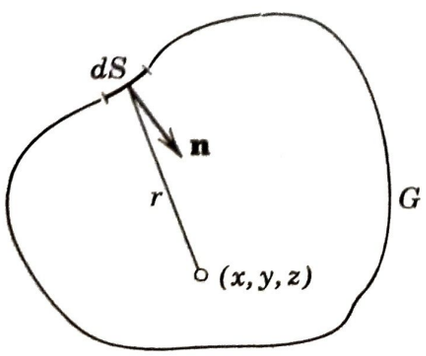

Fig. 1-12. Solution of Poisson's equation in a bounded area.

In recent times the method has been modernized by the application of Dirac's delta function as frequently expressed by some definite integrals. For instance, to obtain the Green function of the Poisson equation

$$\nabla^2\Phi = -4\pi\rho \tag{5.7}$$

we write

$$\nabla^2 G = -4\pi\delta(\mathbf{r}) \tag{5.7a}$$

and take

$$G(\mathbf{r}) = \frac{1}{r}. \tag{5.7b}$$

(More frequently the factor 4π in (5.7*a*) is replaced by unity and (5.7*b*) by $G(r) = 1/4\pi r$.)

The main property of $\delta(\mathbf{r})$ is that it is zero outside of $\mathbf{r} = 0$ or, more strictly, that any volume integral in that region is zero. On the other hand, a volume integral over any region comprising $\mathbf{r} = 0$ is unity. Therefore

$$\int F(\mathbf{r}')\,\delta(\mathbf{r} - \mathbf{r}')\,d\tau' = F(\mathbf{r}). \tag{5.8}$$

The meaning of (5.7*a*) becomes clearer if we write

$$\text{div}\,\nabla G = -4\pi\delta(\mathbf{r}). \tag{5.9}$$

On integrating over a small sphere around $\mathbf{r} = 0$ we have

$$\int \frac{\partial G}{\partial n}\,dS = -4\pi. \tag{5.9a}$$

Using (5.7*b*) for $G(r)$, we have

$$\frac{\partial G}{\partial n} = \frac{\partial G}{\partial r} = -\frac{1}{r^2} \tag{5.9b}$$

and $\int dS = 4\pi r^2$. Hence we obtain the result (5.9*a*).

By means of Green's function (5.7*b*) obeying (5.7*a*) the solution of (5.7) is

$$\Phi(\mathbf{r}) = \int \rho(\mathbf{r}')G(\mathbf{r} - \mathbf{r}')\,d\tau', \tag{5.10}$$

since, applying the Laplace operator, we obtain

$$\begin{aligned}\nabla^2\Phi(\mathbf{r}) &= \int \rho(\mathbf{r}')\nabla^2 G(\mathbf{r} - \mathbf{r}')\,d\tau' \\ &= -4\pi\int \rho(\mathbf{r}')\,\delta(\mathbf{r} - \mathbf{r}')\,d\tau' = -4\pi\rho(\mathbf{r}).\end{aligned} \tag{5.10a}$$

Inserting (5.7*b*), we obtain from (5.10) the well-known formula

$$\Phi(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\tau'. \tag{5.10b}$$

Integral Representation of Green's Function

Among other possible representations the one-dimensional Dirac delta function can be written

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(ix\xi)\, d\xi. \tag{5.11}$$

This gives

$$\int_{-\varepsilon}^{\varepsilon} \delta(x)\, dx = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\exp(i\varepsilon\xi) - \exp(-i\varepsilon\xi)}{\xi}\, d\xi. \tag{5.11a}$$

The value unity of this integral is easily found from the formula

$$\int_{-\infty}^{\infty} \frac{\sin \varepsilon\xi}{\xi}\, d\xi = \int_{-\infty}^{\infty} \frac{\sin x}{x}\, dx = \pi. \tag{5.11b}$$

Most easily it is obtained by deforming the path of integration in (5.11*a*), and next evaluating the terms separately. For instance, let the path of integration have a loop beneath the origin in the complex ξ-plane; the second integral vanishes on closing the path by an infinite semicircle in the lower half-plane. Similarly for the first part of the integral we close the path of integration by a semicircle in the upper half-plane and contract the closed contour around the point $\xi = 0$. Here the integrand has a pole of residue one to be multiplied by $2\pi i$. Hence the result

$$\int_{-\varepsilon}^{\varepsilon} \delta(x)\, dx = 1 \tag{5.12}$$

for any value of ε.

Similarly

$$\int_{\varepsilon_1}^{\varepsilon_2} \delta(x)\, dx = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\exp(i\varepsilon_2\xi) - \exp(i\varepsilon_1\xi)}{\xi}\, d\xi. \tag{5.13}$$

If ε_1 and ε_2 are both positive, the path of integration may be closed in the upper half-plane to give zero for either of the two parts of the integral when directed above the origin. If the path is directed beneath the origin, either of the two parts gives unity and the result is again that

$$\int_{\varepsilon_1}^{\varepsilon_2} \delta(x)\, dx = 0. \tag{5.13a}$$

The three-dimensional δ-function may be transformed as follows:

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^3}\int \exp\,[i(x\xi + y\eta + z\zeta)]\,d\xi\,d\eta\,d\zeta$$

$$= \frac{1}{(2\pi)^3}\int_0^\infty dR\int_0^\pi d\vartheta\int_0^{2\pi} d\varphi R^2 \sin\vartheta \exp\,(iRr\cos\vartheta) \qquad (5.14)$$

upon introducing polar coordinates in the two spaces (x, y, z) and (ξ, η, ζ). Performing the integrations in the angle variables, we obtain the result

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^2 ir}\int_{-\infty}^{\infty} \exp\,(irR)R\,dR. \qquad (5.14a)$$

A formal partial integration, which does not invalidate the character of the expression as a delta function, gives

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^2 r^2}\int_{-\infty}^{\infty} \exp\,(irR)\,dR = \frac{\delta(r)}{2\pi r^2}. \qquad (5.14b)$$

It should be noted that

$$\int_{\infty}^{0} \delta(x)\,dx = \int_0^\infty \delta(x)\,dx = \frac{1}{2}. \qquad (5.14c)$$

Hence with the expression (5.14*b*) for $\delta(r)$,

$$\int \delta(\mathbf{r})\,d\tau = 2\int_0^\infty \delta(\mathbf{r})\,dr = 1 \qquad (5.14d)$$

As to the Green function it is easily found from its differential equation (5.7*a*) to be

$$\dot{\psi} = \frac{4\pi}{(2\pi)^3}\int \frac{\exp\,[i(x\xi + y\eta + z\zeta)]}{\xi^2 + \eta^2 + \zeta^2}\,d\xi\,d\eta\,d\zeta$$

$$= \frac{1}{\pi}\int \exp\,(irR\cos\vartheta)\,dR\sin\vartheta\,d\vartheta$$

$$= \frac{1}{i\pi r}\int_0^\infty \frac{\exp\,(irR) - \exp\,(-irR)}{R}\,dR$$

$$= \frac{2}{\pi r}\int_0^\infty \frac{\sin rR}{R}\,dR = \frac{1}{r}. \qquad (5.15)$$

This only proves the equivalence of different expressions. The method, of course, consists of replacing $1/r$ by some definite integral for the benefit of some integration process. In this respect the Green's method as specialized by

the use of the delta function is more powerful in radiation and scattering theory than in electrostatics.

6. DISTRIBUTION OF CHARGE ON CONDUCTORS

Boundary Conditions for the Potential

In the previous section we have given a proof of the uniqueness of solutions of Laplace's equation for some specified boundary conditions. If the surface or surfaces in question are those of metallic conductors, the boundary conditions are considerably simplified. In particular the condition of given potential values becomes extremely simple because on the surface of a conductor the potential is constant.

The specification of the normal derivative is, however, much more intricate because of its dependence on the curvature of the surface. Even though its surface integral, that is, the integral over the normal component of **E**, or the charge density σ is a well-defined quantity, namely, the total charge on the conductor, this kind of boundary condition should be avoided in preference to the simpler of a given value of the potential.

In our proof of the uniqueness of the solution we used the concept of a region bounded by a closed surface. To this outer boundary may be added any inside conductor surface, since the conductors themselves can be excluded from the domain of integration. The outside surface, on the other hand, may be an infinitely distant surface, in reality partly the surface of the earth. If the potential of this fictitious distant surface is put equal to zero, the solution of the Laplace equation is unique.

Point Charge and Conducting Plane

This is a very simple electrostatic problem from which, however, we can learn basic techniques. Take the metallic surface to be the xy-plane and the point charge to be situated at $z = a$; its proper potential can be set up immediately as

$$\Phi_1 = e\sum_{n=0}^{\infty} P_n(\cos\vartheta)\begin{cases}\dfrac{a^n}{r^{n+1}}, & r > a,\\[2ex] \dfrac{r^n}{a^{n+1}}, & r < a,\end{cases} \tag{6.1}$$

e being the point charge. To this potential, however, must be added the potential of still unknown induced charges on the conducting plane. (See Fig. 1-13.)

To learn what to do we observe that on the plane, with $\vartheta = \frac{1}{2}\pi$, all Legendre polynomials of odd order have zero values and therefore do not invalidate

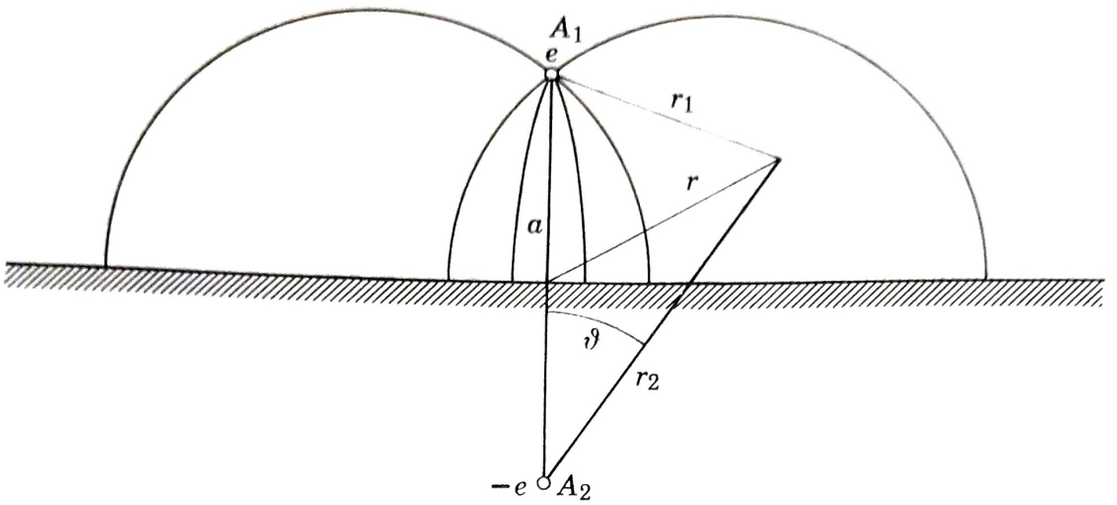

Fig. 1-13. Point charge and conducting plane.

the conditions of the constant potential. Those terms that must be removed on the surface of the conducting plane are the potential of even order. We therefore write

$$\Phi = e\sum_{n=0}^{\infty}[P_n(\cos\vartheta) - P_n(-\cos\vartheta)]\begin{cases}\dfrac{a^n}{r^{n+1}}, & r > a,\\[2ex] \dfrac{r^n}{a^{n+1}}, & r < a.\end{cases} \tag{6.2}$$

Here the latter part is obtained from the first part by changing ϑ into $\pi - \vartheta$. It is evident therefore that the latter sum corresponds to the potential of a charge $-e$ in the image point $z = -a$. Hence

$$\Phi = \Phi_1 + \Phi_2,$$

$$\Phi_1 = \frac{e}{r},$$

$$\Phi_2 = -\frac{e}{r'} = -e\sum_n P_n(-\cos\vartheta)\begin{cases}\dfrac{a^n}{r^{n+1}},\\[2ex] \dfrac{r^n}{a^{n+1}},\end{cases}$$

$$= -e\sum_n (-1)^n P_n(\cos\vartheta)\begin{cases}\dfrac{a^n}{r^{n+1}},\\[2ex] \dfrac{r^n}{a^{n+1}}.\end{cases} \tag{6.3}$$

Hence

$$\Phi = \frac{e}{r} - \frac{e'}{r} \tag{6.3a}$$

with r and r' the distances to the field point from the charge e and its image point, respectively.

Saturation of Electric Lines of Force

A vector field may be illustrated by curves called vector lines or lines of force which at any point in space follow the direction of the field vector. The density of the vector lines as measured by their number per unit area is proportional to the strength of the field. This means that the flux through an area equals the number of vector lines passing through the area. Hence the vector lines emerging from any point or space charge can be broken only by charges of opposite sign. The number of lines of force from a charge e is $4\pi e$; they can end only in opposite charges of sum $-e$, either in some finite region or at infinity.

The above case of a charge and a conducting plane provides an excellent example of a complete saturation of lines of force in an open region.

To find the charge distribution we calculate the field vector $\mathbf{E}$ on the conducting plane, which is bound to be normal to the plane,

$$E_n = -\frac{\partial \Phi}{\partial n} = -\frac{2ea}{R^3} \tag{6.4}$$

with $R = \sqrt{a^2 + \rho^2}$ the distance from e to a circle of radius ρ on the plane. The surface density is obtained upon dividing by 4π. The surface element may be taken to be a circular ring with area $dS = 2\pi\rho\, d\rho$. Hence the total charge on the plane as induced by the point charge e becomes

$$\int \frac{E_n}{4\pi}\, dS = -e\int_0^\infty \frac{a\rho\, d\rho}{(a^2 + \rho^2)^{3/2}} = -e. \tag{6.5}$$

Hence the lines of force from any charge in the half-space are all ending on the conducting plane. The saturation is perfect.

For a closed conducting spherical surface this is obvious. It becomes obvious also for the conducting plane if this is taken to be a degeneration of the spherical surface when its radius is made infinitely large.

It may be of considerable interest to see what happens if the conducting plane is curved to the other side to become the outside surface of a finite conducting sphere.

Point Charge and Conducting Sphere

For convenience we take the origin at the center of the sphere with radius a. Let $R > a$ be the central distance to a point charge e. If $a < r < R$, we may obtain a potential

$$\Phi_1 = \frac{e}{\rho} = e\sum_{n=0}^{\infty} \frac{r^n}{R^{n+1}} P_n(\cos\vartheta), \tag{6.6}$$

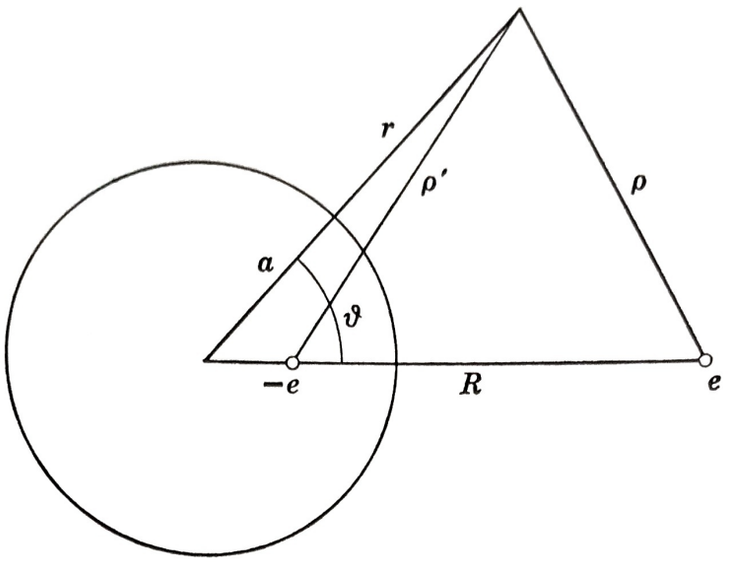

Fig 1-14. Point charge e and conducting sphere.

the unperturbed potential from the point charge. (See Fig. 1-14.)

On the surface of the sphere this potential becomes

$$\Phi_1(a) = e\sum_{n=0}^{\infty} \frac{a^n}{R^{n+1}} P_n(\cos\vartheta). \tag{6.6a}$$

In order that the total potential

$$\Phi = \Phi_1 + \Phi_2 \tag{6.6b}$$

may be constant on the surface, the terms with $n \geqq 1$ in (6.6*a*) must be replaced by the terms of another potential Φ_2 of the form

$$\Phi_2 = -e'\sum_{n=0}^{\infty} \frac{R'^n}{r^{n+1}} P_n(\cos\vartheta) \tag{6.7}$$

which at the surface of the sphere takes the value

$$\Phi_2(a) = -e'\sum_{n=0}^{\infty} \frac{R'^n}{a^{n+1}} P_n(\cos\vartheta). \tag{6.7a}$$

This is the potential of a fictitious charge inside the sphere at a distance $R' < a$. The first condition that all higher terms be eliminated on the sphere is that

$$\frac{R'}{a} = \frac{a}{R} \qquad \text{or} \qquad RR' = a^2, \tag{6.8}$$

which means that $-e'$ is in the image point of e with respect to the spherical surface. Next we must have

$$\frac{e'}{a} = \frac{e}{R} \qquad \text{or} \qquad e' = \frac{a}{R}e. \tag{6.8a}$$

Hence the fictitious charge $-e'$ is smaller than the outside charge e.

If Φ_2 in (6.7) is the only additional potential, the potential on the sphere becomes zero. It corresponds to connecting the sphere to a zero potential which may be that of the earth, from which the sphere is provided with its negative charge.

To find that charge we calculate the normal component of $\mathbf{E}$ on the surface.

$$E_n = -\left(\frac{\partial \Phi}{\partial r}\right)_{r=a}$$

that is,

$$E_n = \sum_{n=0}^{\infty} P_n(\cos \vartheta)\left[-ne\frac{a^{n-1}}{R^{n+1}} - (n+1)e'\frac{R'^n}{a^{n+2}}\right]. \tag{6.9}$$

Here only the zero term contributes to the total charge on the surface,

$$\int \frac{E_n}{4\pi} dS = -\frac{e'}{4\pi a^2} 4\pi a^2 = -e'. \tag{6.9a}$$

As $e' < e$ the lines of force from the point charge e are not saturated on the sphere. Saturation is obtained only by forcing more negative charges into the sphere by connecting it with a negative potential. For instance the potential of a fictitious charge $-(e - e')$ in the center of the sphere gives a normal component of the field vector $-(e - e')/a^2$ corresponding to an even distribution of the fictitious charge on the spherical surface. The corresponding potential on the surface is

$$\Phi_3(a) = -\frac{e - e'}{a}. \tag{6.10}$$

The total potential of a conducting sphere of radius a with a total charge e_0 in the field of a point charge at the central distance $R > a$ becomes

$$\Phi = \frac{e_0 + e'}{r} - \frac{e'}{\rho'} + \frac{e}{\rho}, \qquad e' = e\frac{a}{R} \tag{6.11}$$

with ρ and ρ' the distances to the field point from the point charge and its image point, respectively.

Conducting Sphere in a Homogeneous Field

A homogeneous electric field $\mathbf{E} = -\nabla\Phi$, say, in the z-direction has the potential

$$\Phi_1 = -E_0 z = -E_0 r \cos \vartheta. \tag{6.12}$$

See Fig. 1-15. If a conducting sphere of radius a is placed in this field (with the origin taken at its center) the field is deformed by a second potential Φ_2 which like Φ_1 is a solution of the Laplace equation. In order that the sum be

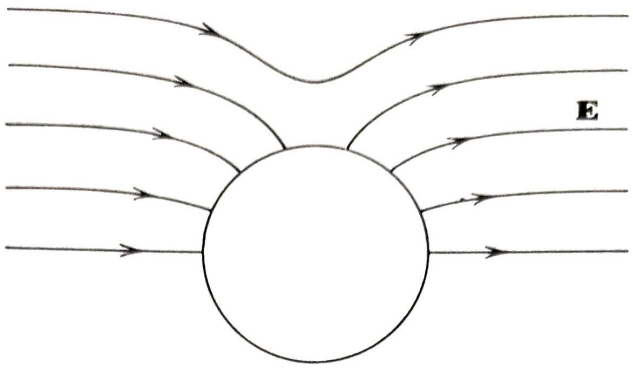

Fig. 1-15. Conducting sphere in homogeneous electric field **E**.

constant on the surface of the sphere, Φ_2 must have the same dependence on the polar angle ϑ. On the other hand, it must decrease with the distance r of the field point from the center of the sphere. Hence there is no other admissible solution than

$$\Phi_2 = C\frac{\cos\vartheta}{r^2} \tag{6.12a}$$

except $\Phi_2 = e/r$ which means that the sphere has a net charge e. The latter possibility is of no particular interest in the above context, since it does not interfere at all with the characteristic result, a polarization of the sphere.

The singularity of Φ_2 at the center of the sphere is, as usual, insignificant, since we are dealing only with the outside field. Inside the sphere the potential is constant and according to (6.6) its value is zero. Adjusting C to being a constant potential on the sphere, which means here zero potential, we have

$$\Phi = E_0\left(\frac{a^3}{r^2} - r\right)\cos\vartheta. \tag{6.13}$$

We may now ask some simple questions, as for instance: What is the surface charge density? This is found by calculating the normal, that is, the radial component of the electric field at $r = a$,

$$\begin{aligned} E_r &= \left(-\frac{\partial\Phi}{\partial r}\right)_{r=a} = 3E_0\cos\vartheta, \\ \sigma &= \frac{1}{4\pi}E_r. \end{aligned} \tag{6.14}$$

This at first does not tell us very much beyond the fact that the sphere becomes positively charged to the right and negatively to the left with net charge zero. It is interesting that this is the only charge distribution that produces a homogeneous field inside the sphere, equal and opposite to the given field. The outside field of course originates from distant sources (for instance, the two plates of a huge plate condenser). To show how this field is

obtained, it may again be simpler to calculate the potential rather than the vector field. Owing to the axial symmetry of the charge distribution and the potential in contrast, for instance, to the spherical symmetry of the potential of an evenly charged sphere surface, the calculation process from the Coulomb law is considerably impeded. On the other hand, we may learn a little from it.

In potential theory we often have to use the expansion theorem

$$P_n(\cos\vartheta_{12}) = \sum_{m=-n}^{n} c_{nm} P_n{}^m(\cos\vartheta_1) P_n{}^m(\cos\vartheta_2) \exp\left[im\,(\varphi_1 - \varphi_2)\right] \quad (6.15)$$

with

$$c_{nm} = \frac{(n - |m|)!}{(n + |m|)!}. \quad (6.15a)$$

Here the angles with indices one and two are polar coordinates of two unit vectors $\mathbf{r}_1{}^0$ and $\mathbf{r}_2{}^0$ and ϑ_{12} is the angle between them:

$$\mathbf{r}_1{}^0\mathbf{r}_2{}^0 = \cos\vartheta_{12} = \cos\vartheta_1 \cos\vartheta_2 + \sin\vartheta_1 \sin\vartheta_2 \cos(\varphi_1 - \varphi_2). \quad (6.16)$$

Let $\mathbf{r}_1$ and $\mathbf{r}_2$ be the corresponding vectors of lengths r_1 and r_2 and r_{12} the distance between their end points. Then $1/r_{12}$ is a solution of the Laplace equation in either of the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$. In the expansion

$$\frac{1}{r_{12}} = \sum_{n=0}^{\infty} \frac{r_1{}^n}{r_2^{n+1}} P_n(\cos\vartheta_{12}), \qquad r_1 < r_2, \quad (6.16a)$$

$P_n(\cos\vartheta_{12})$ is therefore a solution of either of the equations

$$[\nabla_i^{*2} + n(n+1)]P_n(\cos\vartheta_{12}) = 0, \qquad i = 1, 2 \quad (6.16b)$$

with

$$\nabla^{*2} = \frac{\partial^2}{\partial\vartheta^2} + \frac{\cos\vartheta}{\sin\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} \quad (6.16c)$$

the two-dimensional Laplacian of a unit sphere surface. Hence $P_n(\cos\vartheta_{12})$ must be expressed by products of spherical harmonics $P_n{}^m(\cos\vartheta)\exp(\mathrm{i}m\varphi)$ in the two sets of coordinates; since it is a function of $\varphi_1 - \varphi_2$, it must have the form (6.15).

Now since

$$\int_0^{\pi} [P_n{}^m(\cos\vartheta)]^2 \sin\vartheta\, d\vartheta = \frac{2}{2n+1}\frac{(n + |m|)!}{(n - |m|)!}, \quad (6.17)$$

it follows, on squaring (6.15) and integrating over the surface area

$$d\tau_2 = \sin \vartheta_2 \, d\vartheta_2 \, d\varphi_2, \tag{6.17a}$$

that

$$\frac{2n+1}{4\pi} \int \{P_n(\cos \vartheta_{12})\}^2 \, d\tau_2 = 1 = \sum_{m=-n}^{n} \frac{(n+|m|)!}{(n-|m|)!} \, c_{nm}{}^2 [P_n{}^m(\cos \vartheta_1)]^2. \tag{6.18}$$

On the other hand, putting $\vartheta_1 = \vartheta_2$, $\varphi_1 = \varphi_2$ in (6.15), we find

$$1 = \sum_{m=-n}^{n} c_{nm} [P_n{}^m(\cos \vartheta_1)]^2. \tag{6.18a}$$

Comparing the expressions, we find that (6.15*a*) is true.

We now return to the evaluation of the potential of the charge distribution (6.14) at any field point $\mathbf{r}_1$ inside the sphere, using $\mathbf{r}_2$ for the source point coordinates. We then have from (6.14) and (6.16*a*)

$$\frac{\sigma}{r_{12}} = \frac{3E_0 \cos \vartheta_2}{4\pi} \sum_{n=0}^{\infty} \frac{r_1{}^n}{a^{n+1}} P_n(\cos \vartheta_{12}). \tag{6.19}$$

On multiplying with the surface element $a^2 \sin \vartheta_2 \, d\vartheta_2 \, d\varphi_2$ all terms except $n = 1$ give zero. Next from $P_1(\cos \vartheta_{12})$ we need use only $\cos \vartheta_1$, $\cos \vartheta_2$. Integrating, we obtain the result

$$\Phi_2 = \int \frac{\sigma}{r_{12}} \, dS = E_0 r_1 \cos \vartheta_1 = E_0 z, \tag{6.20}$$

that is, just the potential that counterbalances the given potential (6.12).

The final result demonstrated here is merely a fact that is known to be true without proof. It is therefore an indication of the usefulness and simplicity of using differential equations for the solution of physical problems even in cases where more direct calculations may be possible.

A second interesting question is that of the dipole moment of the sphere caused by its surface charge distribution. Again from the expression (6.13)

$$p = E_0 a^3 \tag{6.21}$$

and, moreover, it is a dipole moment in the pure mathematical sense, different from a physical dipole of finite charges e and $-e$ with finite displacement a.

The Charged Circular Disk

On treating the evenly charged rod we found that it was the limiting case of equipotential surfaces of prolate confocal rotational ellipsoids. One might

hope then that a circular disk with evenly distributed surface charge density would produce similarly simple potentials. This is not so. To obtain simple results, in the sense that equipotential surfaces are now oblate rotational ellipsoids, we must consider a conducting disk leaving electric charges free to arrange themselves according to the Laplace solutions of the potentials.

Again we take the z-axis for the symmetry axis, let this be the minor axis of the ellipsoid, and write

$$\frac{x^2 + y^2}{a^2} + \frac{z^2}{b^2} = 1, \qquad b = c\xi, \qquad a = c\sqrt{1 + \xi^2}, \tag{6.22}$$

so that c is the central focal distance of the ellipse cut by a plane through the z-axis. The connection between Cartesian and elliptic coordinates is now

$$\begin{aligned} x &= c[(1 + \xi^2)(1 - \eta^2)]^{1/2} \cos \varphi, \\ y &= c[(1 + \xi^2)(1 - \eta^2)]^{1/2} \sin \varphi, \\ z &= c\xi\eta. \end{aligned} \tag{6.22a}$$

The square line element is

$$ds^2 = c^2\left[\frac{\xi^2 + \eta^2}{1 + \xi^2}\, d\xi^2 + \frac{\xi^2 + \eta^2}{1 - \eta^2}\, d\eta^2 + (1 + \xi^2)(1 - \eta^2)\, d\varphi^2\right]. \tag{6.22b}$$

Hence the volume element

$$d\tau = c^3(\xi^2 + \eta^2)\, d\xi\, d\eta\, d\varphi \tag{6.22c}$$

and the Laplace operator

$$\nabla^2 = \frac{1}{c^2(\xi^2 + \eta^2)}\left[\frac{\partial}{\partial\xi}(1 + \xi^2)\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}(1 - \eta^2)\frac{\partial}{\partial\eta} + \frac{\xi^2 + \eta^2}{(1 + \xi^2)(1 - \eta^2)}\frac{\partial^2}{\partial\varphi^2}\right]. \tag{6.23}$$

The coordinate regions are

$$b < \xi < \infty \qquad -1 < \eta < 1, \qquad 0 < \varphi < 2\pi; \tag{6.23a}$$

$\eta = 0$ is on the equator of the ellipsoid and $\eta = \pm 1$ at the poles.

The only solution of the Laplace equation depending solely on the coordinate ξ is

$$\Phi = \frac{e}{c}\left(\frac{\pi}{2} - \arctan \xi\right) \tag{6.24}$$

if the potential is zero at infinity. The field vector is

$$\mathbf{E} = \frac{e/c}{1+\xi^2}\nabla\xi = \frac{e\hat{\mathbf{s}}}{c^2[(\xi^2+\eta^2)(1+\xi^2)]^{1/2}} \tag{6.24a}$$

with $\hat{\mathbf{s}}$ the unit vector normal to the equipotential surface $\xi = \text{const}$. The surface elements are

$$dS = c^2[(\xi^2+\eta^2)(1+\xi^2)]^{1/2}\,d\eta\,d\varphi. \tag{6.24b}$$

Hence the total surface charge is

$$\int \sigma\,dS = \int \frac{1}{4\pi}\mathbf{E}\hat{\mathbf{s}}\,dS = \frac{e}{4\pi}\int d\eta\,d\varphi = e. \tag{6.25}$$

From (6.24*a*) it is seen that the normal component of **E** for a very thin ellipsoid ($\xi \to 0$) becomes

$$E_n = \frac{e}{c^2\eta}, \tag{6.26}$$

and the surface element

$$dS = c^2\eta\,d\eta\,d\varphi. \tag{6.26a}$$

This means that the surface charge density

$$\sigma = \frac{E_n}{4\pi} = \frac{e}{4\pi c^2\eta} \tag{6.26b}$$

on either side becomes infinite at the edge of the disk,

$$\eta \to 0, \qquad \rho = c(1-\eta^2)^{1/2} \to c.$$

The increase is slow enough, however, to allow for the finite value of the charge e.

The Circular Double Layer

Another quite interesting solution of the Laplace equation in oblate elliptical coordinates is

$$\Phi = 2\pi p\left(1 + \xi\arctan\xi - \frac{\pi}{2}\xi\right)\eta. \tag{6.27}$$

At $\xi = 0$, that is, in a plane circular area of radius c, its value becomes $2\pi p\eta$ with positive and negative sign on either side of the xy-plane. The discontinuity hence is $4\pi p\eta$ or approximately that of a dipole layer of surface density p, except at the edge of the area where it slowly becomes zero. It thus reminds one very much of a circular double layer of constant dipole strength.

To avoid discontinuity of the potential if there is none in the electric field

vector we would have to choose another solution inside some ellipsoidal surface $\xi = \xi_0$. This solution is

$$\Phi = \frac{2\pi p}{\xi_0}\left(1 + \xi_0 \arctan \xi_0 - \frac{\pi}{2}\xi_0\right)\xi\eta, \qquad \xi < \xi_0 \tag{6.28}$$

using the simplest Laplace solution $\xi\eta$.

The outside potential decreases from $\xi = \xi_0$ to infinity, where it takes the value zero. Similarly the inside potential decreases inward to the zero value at $\xi = 0$. To maintain the discontinuity at the boundary surface a charge density is needed, which we are now going to calculate.

The normal component of **E** is

$$E_n = -\frac{\partial\Phi}{\partial\xi}\frac{\partial\xi}{\partial s}, \qquad \frac{\partial\xi}{\partial s} = \frac{1}{c}\left(\frac{1+\xi^2}{\xi^2+\eta^2}\right)^{1/2}. \tag{6.29}$$

The surface charge density hence becomes

$$\sigma = \frac{E_{n1} - E_{n2}}{4\pi} = \frac{p}{2}\left(\frac{1}{\xi_0} - \frac{\xi_0}{1+\xi_0^2}\right)\eta. \tag{6.29a}$$

As $\xi_0 \to 0$ the field becomes practically linear, although extremely strong, namely, $4\pi p\eta/2\xi_0$. On the other hand, the gap between the two surfaces of opposite charge density becomes $2\xi_0/\eta$. Hence the potential difference is $4\pi p$, as it should be.

The above case does not, unfortunately, apply to the circular plate condenser with conducting circular plates, which is a still more intricate problem.

7. DIELECTRICS AND POLARIZATION

Space Dipole Density of Polarization

We have seen that a physical dipole in the sense of two finite charges e and $-e$ separated by a distance a produces a series of multipoles of the form $(ea^n/r^{n+1})P_n(\cos\vartheta)$. If a is small enough in comparison to the distance r to the field point, we are left only with the first term, that is, a dipole in the purely mathematical sense, defined by the vector $\mathbf{p} = e\mathbf{a}$.

By some process atomic or molecular dipoles may be formed in matter in bulk and even become suitably orientated so as to provide infinitesimal regions in space with an electric dipole moment. Those regions that in the macroscopic picture may be thought of as infinitesimal will still contain an enormous number of minute atomic or molecular dipoles. These dipoles may be summed up to a definite value of the dipole moment for any small volume element. Thus we are led to the concept of electric dipole density in what are

called dielectric bodies or dielectrics. This quantity we denote by a vector **P**, the polarization vector.

This vector, of course, may be—and in fact has been—introduced as a phenomenological quantity expressing a displacement of, say, positive electric charges out from their normal position where on the average they are neutralized by corresponding negative charges, or vice versa. The dimension of polarization therefore is the transport of electricity or rather the charge density, that is, electric charge density times length.

The electrostatic potential of a piece of matter in the state of given polarization is

$$\Phi = \int \frac{\mathbf{Pr}}{r^3}\, d\tau \tag{7.1}$$

with **r** as usual the vector from the source to the field point as an abbreviation for, say, $\mathbf{r} - \mathbf{r}'$ in an arbitrary frame and with $d\tau$ for $d\tau' = d^3x'$.

We now use the expression

$$\operatorname{div} \frac{\mathbf{P}}{r} = \frac{\operatorname{div} \mathbf{P}}{r} + \frac{\mathbf{Pr}}{r^3} \tag{7.2}$$

with div relating to the source point, to replace (7.1) by

$$\Phi = \int \left(\operatorname{div} \frac{\mathbf{P}}{r} - \frac{\operatorname{div} \mathbf{P}}{r} \right) d\tau. \tag{7.3}$$

Next we apply the formula to a finite piece of matter to obtain by the Gauss theorem the significant formula of the Coulomb type:

$$\Phi = \int \frac{\sigma'\, dS}{r} + \int \frac{\rho'}{r}\, d\tau \tag{7.4}$$

with

$$\sigma' = P_n, \qquad \rho' = -\operatorname{div} \mathbf{P}. \tag{7.4a}$$

The quantities of (7.4*a*), which are called surface and space density of free charges or fictitious charges are easily interpreted. The latter is an expression for the conservation of electric charges, that is, the continuity equation. If the polarization **P**, the displacement of electric charges, is nonuniform, the result must be the accumulation of charges of one or the other sign to a definite space density distribution.

Similarly a polarization vector of unit strength may be thought of as corresponding to a unit positive and a unit negative charge on the front and the back, respectively, of a unit cube. If a number of such cubes are lined up in a row, the effect will be as though a unit surface charge density existed at

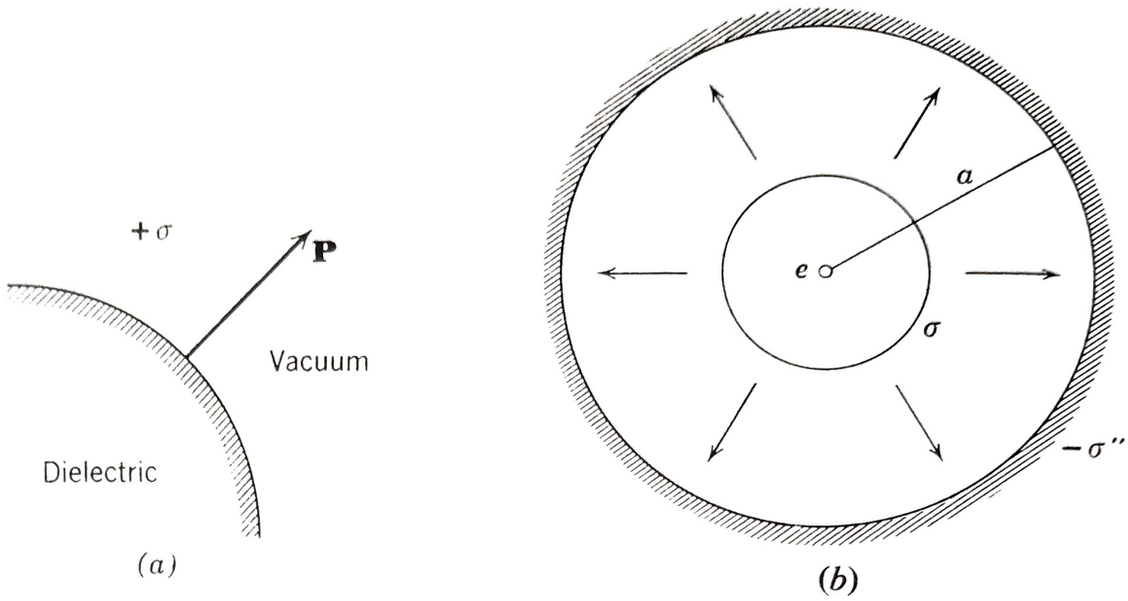

Fig. 1-16(*a*). Free charge on a dielectric surface. (*b*) Shielding effect on true charges by free charges in dielectrica explaining the reduced Coulomb field $e/\varepsilon r$.

either end of the row. Therefore P_n represents a true surface charge density as denoted by σ'.

Even though both ρ' and σ' are true enough, as expressed also by the Coulomb potential (7.4), they are called free charges, or even fictitious charges, to be distinguished from "true" charges produced on the surface of a conductor or on the surface or in the interior of an insulator. By definition, then, free charges are produced by polarization and disappear when polarizing forces are removed. See Figs. 1-16*a* and 1-16*b*.

In the presence of true charges we write ρ'' and σ'' for the fictitious or polarization charges, reserving the notation ρ' and σ' for the sum of charges responsible for the Coulomb field. Hence in the equation

$$\operatorname{div} \mathbf{E} = 4\pi\rho' \tag{7.5}$$

we write

$$\rho' = \rho + \rho'' = \rho - \operatorname{div} \mathbf{P}. \tag{7.5a}$$

On introducing the auxiliary vector

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}, \tag{7.6}$$

called the displacement, we have

$$\operatorname{div} \mathbf{D} = 4\pi\rho. \tag{7.6a}$$

Hence in the presence of dielectrics the displacement **D** takes up the former role of **E**. Still it is **E** that is the potential gradient $\mathbf{E} = -V\Phi$ with the property

$$\operatorname{curl} \mathbf{E} = 0. \tag{7.6b}$$

Electric Susceptibility and Polarizability. The Dielectric Constant

The polarization of dielectrics is not a static state of matter but is caused by external forces, whether by true polarization of atoms or by the partial orientation of molecules with permanent dielectric moments. The cause of the polarization hence is the external electric field, and the simplest law for the dependence is the linear relation

$$\mathbf{P} = \kappa \mathbf{E}. \tag{7.7}$$

The material constant κ is called the electric susceptibility of the dielectric. In its most general form κ is a quantity with several components, a symmetric tensor. The anisotropy of a medium as expressed by such a tensor belongs to the realm of crystal optics and will not be dealt with here. We simply consider only isotropic dielectrics for which κ is a scalar material constant.

Also the displacement vector $\mathbf{D}$ depends linearly on $\mathbf{E}$,

$$\mathbf{D} = \varepsilon \mathbf{E}, \qquad \varepsilon = 1 + 4\pi\kappa. \tag{7.7a}$$

Finally we must make a distinction between the mean or macroscopic electric field as expressed by $\mathbf{E}$, and the polarizing field $\mathbf{E}_0$ really acting on individual atoms and molecules. (See Fig. 1-17.)

The field produced by a single atom does not react with the atom itself, and the mean force from a number of neighboring atoms is zero in virtue of the random arrangement. Therefore we may calculate the field $\mathbf{E}_0$ by neglecting the effect of neighboring matter within a sphere around the atom. That this is a reliable procedure is confirmed by the fact that the calculated effect is independent of the radius of the sphere.

Take the origin to be in the center of the spherical cavity of radius a and let the z- or ϑ-axis be in the direction of the field. The surface charge density

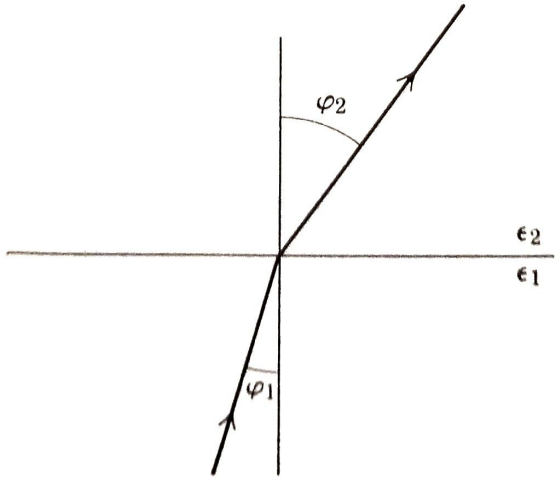

Fig. 1-17. Refraction of electric field lines on the border of different dielectrics.

on the inner side of the sphere will be $-P\cos\vartheta$. In the center of the sphere this gives a field component

$$dE'' = \frac{P}{a^2}\cos^2\vartheta\, a^2 \sin\vartheta\, d\varphi \tag{7.8}$$

in the direction of the field **E**, or, when integrated,

$$E'' = \frac{4\pi}{3}P. \tag{7.8a}$$

We now define another quantity, namely, the polarizability α per atom or molecule, by the equation

$$\mathbf{P} = N\alpha(\mathbf{E} - \mathbf{E}'') = N\alpha\left(\mathbf{E} + \frac{4\pi}{3}\mathbf{P}\right) \tag{7.9}$$

with N the number of polarized particles per unit volume. This gives the susceptibility

$$\kappa = \frac{N\alpha}{1 - (4\pi/3)N\alpha} \tag{7.9a}$$

and the inverse formula

$$N\alpha = \frac{\kappa}{1 + (4\pi/3)\kappa}. \tag{7.9b}$$

Multiplying by $4\pi/3$ and eliminating κ, we find

$$\frac{4\pi}{3}N\alpha = \frac{\varepsilon - 1}{\varepsilon + 2}. \tag{7.9c}$$

The formula is called the Clausius-Mosotti formula as found by Mosotti (1850) and by Clausius (1879). As $\varepsilon \to 1$ it becomes approximately

$$4\pi N\alpha = \varepsilon - 1. \tag{7.9d}$$

For larger values of ε, as we shall soon see, the validity of the formula may to some extent be doubted.

Dielectric Sphere in a Homogeneous Field. Spherical Cavity in a Dielectric

The two problems may be treated simultaneously by considering an outer and an inner dielectric with dielectric constants ε_e and ε_i, respectively. Because of curl **E** = 0, div **D** = 0 the boundary conditions become: continuity of the tangential component E_t and the normal component D_n. The former condition is already fulfilled by the requirement that the electrostatic potential be continuous. (See Fig. 1-18.)

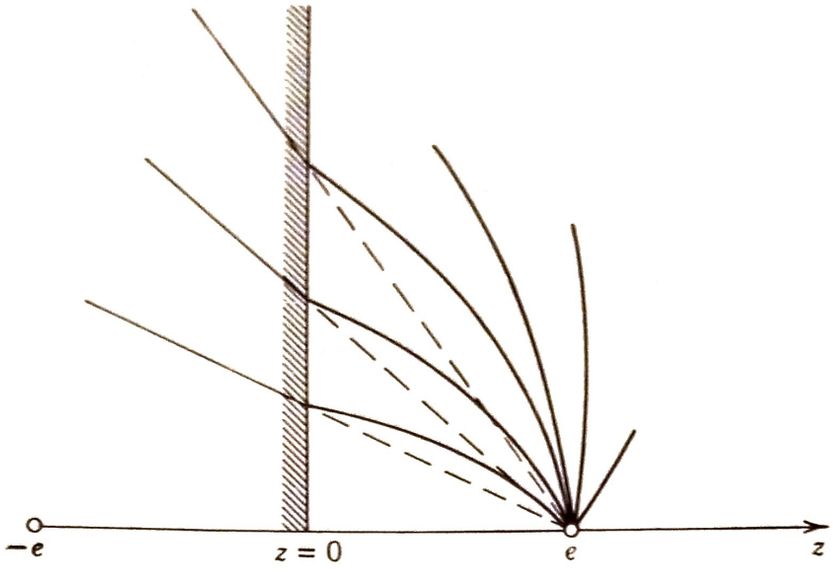

Fig. 1-18. Point charge and dielectric half-space.

Taking the outer and inner potentials to be of the form

$$\Phi = -Er\cos\vartheta + \frac{p}{r^2}\cos\vartheta,$$
$$\Phi' = -E'r\cos\vartheta, \tag{7.10}$$

we obtain for a sphere of radius a the condition for the continuous potential

$$E - E' = \frac{p}{a^3}. \tag{7.10a}$$

Using $\mathbf{D} = \varepsilon\mathbf{E} = -\varepsilon\nabla\Phi$, the condition for continuous D_n or D_r reads

$$\varepsilon_e E - \varepsilon_i E' = -2\varepsilon_e \frac{p}{a^3}. \tag{7.10b}$$

Hence by elimination of the right-hand sides

$$E' = \frac{3\varepsilon_e}{2\varepsilon_e + \varepsilon_i} E. \tag{7.11}$$

Taking first the case of the dielectric sphere in vacuum, $\varepsilon_e = 1$, $\varepsilon_i = \varepsilon$, we have

$$E' = \frac{3}{2+\varepsilon} E \tag{7.12}$$

and

$$D' = \frac{3\varepsilon}{2+\varepsilon} D. \tag{7.12a}$$

The representation of the field by the displacement vector $\mathbf{D}'$ inside and

$\mathbf{D} = \mathbf{E}$ outside the sphere may be preferred because of its divergence-free (solenoidal) character which makes the displacement vector lines unbroken. The lines of force are then seen to be drawn toward the dielectric and partly captured. The displacement field is stronger inside than outside the sphere, whereas the electric field is weakened.

In the spherical cavity of a dielectric, $e_e = \varepsilon$, $\varepsilon_i = 1$, we have, on the other hand,

$$E' = \frac{3\varepsilon}{2\varepsilon + 1} E \tag{7.13}$$

and

$$D' = \frac{3}{2\varepsilon + 1} D, \tag{7.13a}$$

which means that the unbroken displacement vector lines are avoiding the cavity. Nevertheless the electric field changes the opposite way and is strengthened.

From (7.13) it follows that the additional electric field inside the cavity is

$$E'' = E' - E = \frac{\varepsilon - 1}{2\varepsilon + 1} E = \frac{4\pi}{2\varepsilon + 1} P \tag{7.14}$$

and hence that the evaluation of E'' in (7.8a), the basis of the Clausius-Mosotti formula, is fallacious. This, of course, is due to the removal of polarizable matter in the cavity, which has not been taken into account.

Now let us consider a single dipole of strength p in the direction of $\mathbf{E}$ placed in the center of the cavity. It is not quite true that it has no reaction on itself. Polarizing the outside dielectric causes a separate electric field with inside and outside potentials

$$\varphi_i = \frac{p}{r^2} \cos \vartheta - E_i'' r \cos \vartheta, \qquad \varphi_e = \frac{p_e}{r^2} \cos \vartheta. \tag{7.15}$$

The boundary conditions lead to the result

$$E_i'' = \frac{2(\varepsilon - 1)}{2\varepsilon + 1} \frac{p}{a^3}, \tag{7.15a}$$

and this represents a real additional force to the self-potential. If p equals the dipole moment

$$p = \frac{4\pi}{3} a^3 P \tag{7.15b}$$

of the sphere when refilled with the dielectric, we have, using (7.14), the

result

$$E'' + E_i'' = \frac{4\pi}{2\varepsilon + 1} P\left(1 + \frac{2(\varepsilon - 1)}{3}\right) = \frac{4\pi}{3} P \qquad (7.15c)$$

corresponding to (7.8*a*) and the Clausius-Mosotti formula.

Hence it is difficult to see to what extent the Clausius-Mosotti formula may be trusted. Its possible failure is at least restricted to dense matter.* See Figs. 1-19*a* and 1-19*b*.

8. ELECTRODYNAMICS

Potential and Potential Energy of Electric Charges. Field Energy in Dielectrics

On applying the Gauss theorem to the differential equation div $\mathbf{D} = 4\pi\rho$ it is found that the flux of $\mathbf{D}$ through a closed surface equals the inside total charge e. This means that for a point charge in a homogeneous dielectric we have

$$\mathbf{D} = \frac{e}{r^2}\mathbf{r}^0, \qquad \mathbf{E} = \frac{e}{\varepsilon r^2}\mathbf{r}^0, \qquad \mathbf{r}^0 = \frac{\mathbf{r}}{r}. \qquad (8.1)$$

The weakening of $\mathbf{E}$ in the dielectric is puzzling because it announces a breakdown of the Coulomb law and we do not see the reason for it. The correctness of the Coulomb law is clearly restored if we cut away a small sphere of dielectric around the point charge e. Then an amount of fictitious charge e'' is induced on the inside spherical border of the dielectric leaving in the inner region a total free charge

$$e' = e + e'' = \frac{e}{\varepsilon} \qquad (8.1a)$$

which is in fact a true charge in the real sense.

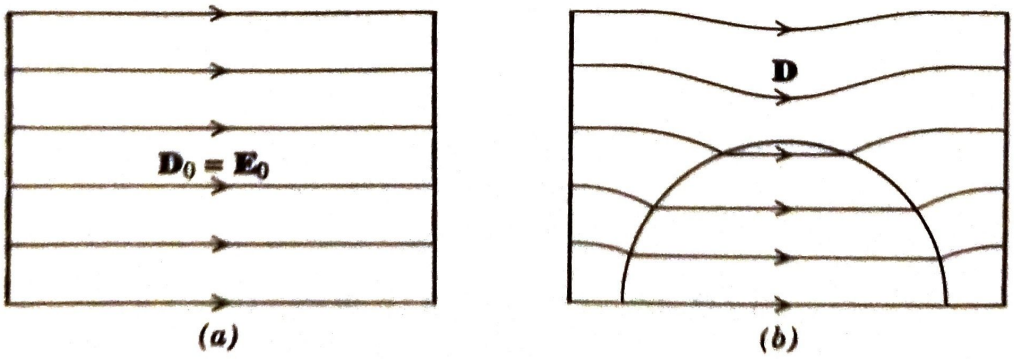

Fig. 1-19. ((*a*) Homogeneous electric field. (*b*) Homogeneous electric field distorted by a dielectric sphere.

* This question has been discussed in detail by Onsager et al., 1956, *Handb. d. Phys.*, Vol. VII, p. 50.

The potential of the point charge becomes

$$\Phi = \frac{e}{\varepsilon r} \tag{8.2}$$

and the mutual potential energy of two charges e_1 and e_2 is

$$U_{12} = \frac{e_1 e_2}{\varepsilon r_{12}} \tag{8.3}$$

or

$$U_{12} = e_1\Phi_1 = e_2\Phi_2 = \tfrac{1}{2}(e_1\Phi_1 + e_2\Phi_2) \tag{8.3a}$$

if by Φ_i we denote the potential at e_i as produced by one or more charges e_k. For a number of charges the potential energy becomes

$$U = \frac{1}{2}\sum_{i \neq k} \frac{e_i e_k}{\varepsilon r_{ik}} = \frac{1}{2}\sum_i e_i\Phi_i, \tag{8.3b}$$

and for a continuous charge distribution

$$U = \frac{1}{2}\int \rho\Phi \, d\tau. \tag{8.4}$$

To insure the correctness of this formula in the case of spatially variable dielectric constant ε, or with regions of different ε, we consider electric charges gradually brought into position in proportion to the final distribution ρ. The charge density then at a given stage is $\lambda\rho$ and the electrostatic potential correspondingly $\lambda\Phi$. On increasing the charge by $d\rho = \rho \, d\lambda$ the potential energy increases by the corresponding amount

$$dU = \int (\rho \, d\lambda)\Phi \, d\tau = \lambda \, d\lambda \int \rho\Phi \, d\tau. \tag{8.4a}$$

Hence, adding up from $\lambda = 0$ to $\lambda = 1$, we obtain the result of (8.4).

In the expression (8.4) we now write

$$\rho = \frac{1}{4\pi} \operatorname{div} \mathbf{D} \tag{8.5}$$

and apply the equation

$$\operatorname{div} (\mathbf{D}\Phi) = \mathbf{D} \operatorname{grad} \Phi + \Phi \operatorname{div} \mathbf{D} \tag{8.5a}$$

to obtain by $\operatorname{grad} \Phi = -\mathbf{E}$ and by the Gauss theorem

$$U = \frac{1}{8\pi}\int \mathbf{E}\mathbf{D} \, d\tau + \frac{1}{8\pi}\int \Phi D_n \, dS. \tag{8.6}$$

The surface integral may be thought of as taken over a distant closed surface with small values of Φ and even smaller of D_n. In fact, if all charges are kept within a finite volume, Φ and D_n will decrease with the powers r^{-1} and r^{-2} of some length r related to the mean distance of the surface from a point in the region of the charges. The total surface then increases as r^2, so that finally for an infinitely remote surface we are left with the expression

$$U = \frac{1}{8\pi} \int \mathbf{ED}\, d\tau. \tag{8.6a}$$

This is a curious result because it localizes the energy in the field rather than in the charges. We shall not be too concerned with the ultimate meaning of the statement but simply note that we may imagine an energy density

$$u = \frac{1}{8\pi} \mathbf{ED} \tag{8.6b}$$

being present in any electric field.

To complete the consideration we shall also add to the expression (8.4) of the potential energy contributions from surface charges on conductors, or even better, go the other way from (8.6*a*). Using (8.5) and (8.5*a*), we write

$$\mathbf{ED} = -\text{div}\,(\Phi\mathbf{D}) + 4\pi\rho\Phi \tag{8.7}$$

to find

$$U = \frac{1}{2} \int \rho\Phi\, d\tau - \frac{1}{8\pi} \int \Phi D_n\, dS, \tag{8.8}$$

where the surface integral now relates to boundaries of the field on metallic conductors with D_n the normal component pointing to the inside of the conductor. Hence with $D_n = -4\pi\sigma$ the result is

$$U = \frac{1}{2} \int \rho\Phi\, d\tau + \frac{1}{2} \int \Phi\sigma\, dS. \tag{8.9}$$

Because of the constancy of the potential Φ on conductors we may write

$$\frac{1}{2} \int \Phi\sigma\, dS = \frac{1}{2} e\Phi \tag{8.9a}$$

for a single conductor and

$$U = \frac{1}{2} \int \rho\Phi\, d\tau + \frac{1}{2} \sum_i e_i\Phi_i \tag{8.9b}$$

for an arbitrary number of conductors.

Mechanical Forces in Dielectrics

The mechanical force on a point charge in an electrostatic field is by definition

$$\mathbf{F} = e\mathbf{E}. \tag{8.10}$$

For a continuous charge distribution we may write correspondingly

$$d\mathbf{F} = \mathbf{E}\rho\, d\tau \tag{8.10a}$$

for the force on the total charge in any minute volume element. It is customary to refer this force to the unit volume and write

$$\mathbf{F} = \rho\mathbf{E}. \tag{8.11}$$

This force refers merely to the possible motion of electric charges and connects the work performed on displaced charges with the decrease of potential or field energy:

$$\delta A = -\delta U. \tag{8.12}$$

When the charge distribution is arbitrarily changed by amounts $\delta\rho$ per unit volume, the potential energy is changed by a total amount of

$$\delta U = \int \Phi\, \delta\rho\, d\tau. \tag{8.13}$$

In order to be able to refer the change to individual charge elements we write

$$\delta\rho = -\operatorname{div}(\rho\, \delta\mathbf{q}) \tag{8.13a}$$

where $\delta\mathbf{q}$ represents arbitrary displacements of the charges. Inserting (8.13*a*) in (8.13) and writing

$$\Phi \operatorname{div}(\rho\, \delta\mathbf{q}) = \operatorname{div}(\Phi\rho\, \delta\mathbf{q}) - \rho\, \delta\mathbf{q}\nabla\Phi, \tag{8.13b}$$

we obtain

$$\delta U = \int (\rho\, \nabla\Phi)\, \delta\mathbf{q}\, d\tau \tag{8.14}$$

on the supposition that the volume integral of the divergence may be transformed into a surface integral over some distant surface. Comparing (8.14) with

$$\delta A = \int \mathbf{F}\, \delta\mathbf{q}\, d\tau \tag{8.14a}$$

and using (8.12) the result must be, as stated in (8.11),

$$\mathbf{F} = -\rho\nabla\Phi = \rho\mathbf{E} \tag{8.14b}$$

because of the arbitrariness of $\delta\mathbf{q}$.

To find the forces on the dielectric medium itself we have to allow for a displacement of the dielectric as well. We now take the standpoint of expressing the energy of the system in terms of the field energy

$$U = \frac{1}{8\pi}\int \mathbf{ED}\, d\tau = \frac{1}{8\pi}\int \frac{\mathbf{D}^2}{\varepsilon}\, d\tau \tag{8.15}$$

whence

$$\delta U = \frac{1}{4\pi}\int \mathbf{E}\,\delta\mathbf{D}\, d\tau - \frac{1}{8\pi}\int \mathbf{E}^2\,\delta\varepsilon\, d\tau. \tag{8.15a}$$

Now because of

$$\operatorname{div}\delta\mathbf{D} = \delta \operatorname{div}\mathbf{D} = -4\pi\,\delta\rho = -4\pi \operatorname{div}(\rho\,\delta\mathbf{q}) \tag{8.15b}$$

we may assume

$$\delta\mathbf{D} = -4\pi\rho\,\delta\mathbf{q}. \tag{8.15c}$$

Similarly in order to avoid any change of individual properties of the volume elements of the dielectric, we have to assume divergence-free displacements $\delta\mathbf{q}$ whence

$$\delta\varepsilon = -\operatorname{div}(\varepsilon\,\delta\mathbf{q}) = -\delta\mathbf{q}\nabla\varepsilon. \tag{8.15d}$$

Equation 8.15*a* is then turned into

$$\delta U = -\int\left\{\rho\mathbf{E} - \frac{1}{8\pi}\mathbf{E}^2\nabla\varepsilon\right\}\delta\mathbf{q}\, d\tau, \tag{8.16}$$

from which as in (8.14) and (8.14*a*) we derive the volume force

$$\mathbf{F} = \rho\mathbf{E} - \frac{1}{8\pi}\mathbf{E}^2\nabla\varepsilon. \tag{8.17}$$

The Maxwell Stress Tensor

In practice we more frequently have to deal with abrupt changes of ε on the border of homogeneous dielectrics. In modifying the last term of (8.17) into a surface force per unit area of the border we have to proceed with some care.

For simplicity let the outside space be empty with $\varepsilon = 1$ and let the positive normal be that pointing to empty space. On remembering that E_t and D_n are continuous we find by integration through an infinitesimal layer of varying ε the surface force

$$\mathbf{F} = \frac{\mathbf{n}}{8\pi}\left(E_t^2 + \frac{1}{\varepsilon}D_n^2\right)(\varepsilon - 1). \tag{8.18}$$

It proves impossible to interpret the above surface force and even the corresponding volume force of (8.17) in any satisfactory way by the static picture of electric fields acting on electric charges. This demonstrates very convincingly the necessity of applying the energy principle and the concept of virtual displacements.

The best method, therefore, is to change the volume forces of (8.17) into surface forces acting on any boundary of a substance or even formally on any surface in space. This procedure leads to the famous Maxwell stress tensor which is intimately connected with the field concept or the concept of point to point transmission of electric forces. In this modified treatment the somewhat dubious term in (8.17) containing $\nabla\varepsilon$, hence referring to material properties, proves to contribute just what is needed in order to obtain the Maxwell tensor in ideal form. (See Fig. 1-20.)

Let us write the x-component of (8.17) in the form

$$\begin{aligned} 8\pi F_x &= 2E_x \operatorname{div} \mathbf{D} - \mathbf{E}^2 \frac{\partial \varepsilon}{\partial x} \\ &= \operatorname{div} 2E_x\mathbf{D} - 2\mathbf{D}\nabla E_x - \mathbf{E}^2 \frac{\partial \varepsilon}{\partial x} \\ &= \operatorname{div} (2\varepsilon E_x\mathbf{E} - \mathbf{i}\varepsilon\mathbf{E}^2), \end{aligned} \tag{8.19}$$

where $\mathbf{i}$ is the unit vector in the direction of the x-axis. The formula is easily proved by remembering that curl $\mathbf{E} = 0$, that is, $\partial E_y/\partial x = \partial E_x/\partial y$, and so on. Writing

$$\mathbf{T}_x = \frac{1}{8\pi}(2\varepsilon E_x\mathbf{E} - \mathbf{i}\varepsilon\mathbf{E}^2), \tag{8.19a}$$

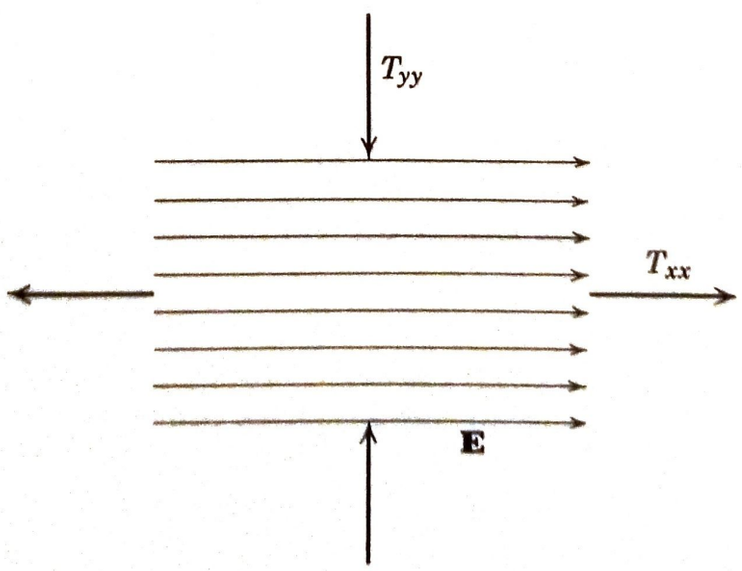

Fig. 1-20. Maxwell's tensor forces.

we obtain by the Gauss theorem

$$\int F_x \, d\tau = \int \mathbf{n}\mathbf{T}_x \, dS. \tag{8.20}$$

This means that the volume integral of any space force component can be transformed into a surface integral over a surrounding boundary. Hence we may write for the vectorial force integral

$$\int \mathbf{F} \, d\tau = \int [(\mathbf{n}\mathbf{T}_x)\mathbf{i} + (\mathbf{n}\mathbf{T}_y)\mathbf{j} + (\mathbf{n}\mathbf{T}_z)\mathbf{k}] \, dS. \tag{8.20a}$$

The equation states that the total force on a finite volume in space may be interpreted as summed up from surface forces acting on its boundary. The surface forces can be represented by a dyadic or tensor for which we write

$$T = \mathbf{T}_x \cdot \mathbf{i} + \mathbf{T}_y \cdot \mathbf{j} + \mathbf{T}_z \cdot \mathbf{k}, \tag{8.21}$$

using the point for dyadic multiplication, that is, as a sign of avoiding scalar multiplication for which the simpler expression **AB**, and so forth, is used.

Equation 8.20*a* then takes the form

$$\int \mathbf{F} \, d\tau = \int \mathbf{n}T \, dS, \tag{8.22}$$

where $\mathbf{n}T$ means scalar multiplication, the product being a vector.

In dyadic products the order of factors is essential. In the above case, however, the resulting Maxwell tensor is symmetric and the order of dyadic factors may be changed. Introducing the identity tensor

$$I = \mathbf{i} \cdot \mathbf{i} + \mathbf{j} \cdot \mathbf{j} + \mathbf{k} \cdot \mathbf{k}, \tag{8.23}$$

the Maxwell tensor reads

$$T = \frac{1}{8\pi} [2\mathbf{E} \cdot \mathbf{D} - I(\mathbf{ED})]. \tag{8.23a}$$

Surface Forces on Discontinuities

In the direction of vector lines the Maxwell tensor corresponds to a stress, and in perpendicular direction to a pressure. To see this take the field in the z-direction to obtain

$$T = \frac{E\,D}{8\pi} [\mathbf{k} \cdot \mathbf{k} - (\mathbf{i} \cdot \mathbf{i} + \mathbf{j} \cdot \mathbf{j})]. \tag{8.23b}$$

With $\mathbf{n} = \mathbf{k}$ we then have $\mathbf{n}T = \mathbf{k}ED/8\pi$ and with $\mathbf{n} = \mathbf{i}$ we have $\mathbf{n}T = -\mathbf{i}ED/8\pi$, and so forth.

The result as given in (8.18) is easily proved. With **E** and **D** in the normal direction there is a stress to either side resulting in

$$F' = \frac{1}{8\pi}[(ED)_{\varepsilon=1} - (ED)_{\varepsilon}] = \frac{D^2}{8\pi}\left(1 - \frac{1}{\varepsilon}\right) \tag{8.24}$$

and similarly with **E** and **D** parallel to the border surface

$$F' = \frac{1}{8\pi}[(ED)_{\varepsilon} - (ED)_{\varepsilon=1}] = \frac{E^2}{8\pi}(\varepsilon - 1). \tag{8.24a}$$

Another example is the stress in normal direction to a charged metallic surface. Inside the metal there is no field and no stress. Outside the stress becomes

$$T_{nn} = \frac{1}{8\pi} D_n E_n = \frac{1}{2}\sigma E_n \tag{8.25}$$

which may be interpreted as the charge σ per unit area times the mean value of the outside and inside electric field. (See Figs. 1-21*a* and 1-21*b*.)

The result can be used to illustrate the transformation of mechanical work into electrostatic field energy. Consider a plate condenser with one movable plate to regulate the plate distance.

The movable plate has a given charge $e = S\sigma$ with given charge density σ on the plate area S. The other plate is kept to a given potential, say, $V = 0$ and is automatically provided with a charge density $-\sigma$.

If the gap is filled with a gas or a liquid with dielectric constant ε, we have

$$D_n = \varepsilon E_n, \qquad \sigma = \frac{1}{4\pi} D_n. \tag{8.26}$$

The force on the movable plate in the direction of the other plate is

$$F_n = \tfrac{1}{2}\sigma E_n S = \tfrac{1}{2} e E_n, \tag{8.26a}$$

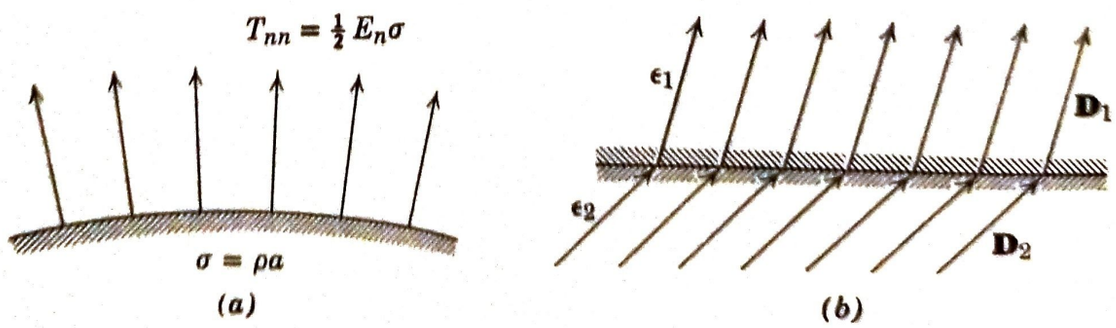

Fig. 1-21. (*a*) Stress on a charged metallic surface. (*b*) Modified shape of the field on dielectric borders.

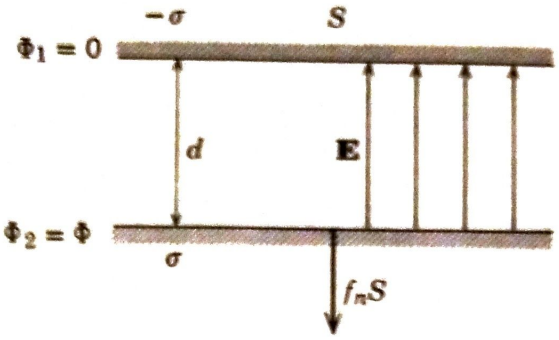

Fig. 1-22. Energy in a plate condenser field produced by mechanical work.

and this is the force that must be applied in the opposite direction to move the plate from zero to a finite plate distance d. Hence the mechanical work spent on separating the plates is

$$W = \tfrac{1}{2} e E_n a = \tfrac{1}{2} e \Phi, \tag{8.26b}$$

where $\Phi = aE_n$ is the produced potential difference. (See Fig. 1-22.)

This is the electrostatic energy in the Coulomb sense. Now put $e = \sigma S$ and use (8.26) to eliminate σ, thus obtaining

$$W = \frac{1}{2} \sigma E_n S a = \frac{1}{8\pi} D_n E_n \tau, \tag{8.26c}$$

where $\tau = Sa$ is the volume between the plates in which the new electrostatic field has been created.

Energy Minimum of the Electrostatic Field. Kelvin's Theorem

The electrostatic field is the field distribution that makes field energy an absolute minimum. This result is known as Kelvin's theorem and applies to any inhomogeneous dielectric together with a system of conductors with given charges $e_1, e_2, \cdots$. Discontinuities of the dielectric, however, need not be considered separately because they may be thought of as rapid variations of the dielectric constant in a thin layer along the discontinuities.

The connections between field quantities and charge are

$$\mathbf{D} = \varepsilon \mathbf{E}, \tag{8.27}$$

$$\operatorname{div} \mathbf{D} = 4\pi\rho, \qquad \int D_n \, dS_k = 4\pi e_k, \tag{8.27a}$$

the latter equation referring to any of the conductors k.

We now put

$$U = \frac{1}{8\pi}\int \mathbf{ED}\, d\tau = \min \tag{8.28}$$

and

$$\delta U = \frac{1}{8\pi}\int (\mathbf{E}\,\delta\mathbf{D} + \delta\mathbf{E}\mathbf{D})\, d\tau = 0, \tag{8.28a}$$

where $\delta\mathbf{E}$ and $\delta\mathbf{D}$ are arbitrary variations of the field apart from the restrictions given in (8.27) and (8.27*a*). From (8.27) it follows that the two terms of the integrand are equal. Hence

$$\delta U = \frac{1}{4\pi}\int \mathbf{E}\,\delta\mathbf{D}\, d\tau = 0, \tag{8.28b}$$

where in addition we have from (8.27*a*)

$$\operatorname{div}\delta\mathbf{D} = 0, \qquad \int \delta D_n\, dS_k = 0. \tag{8.28c}$$

If now $\mathbf{E}$ is the electrostatic field in the sense of being expressible by a potential Φ,

$$\mathbf{E} = -\nabla\Phi, \tag{8.29}$$

we have

$$\mathbf{E}\,\delta\mathbf{D} = -\operatorname{div}\Phi\,\delta\mathbf{D}. \tag{8.29a}$$

Hence

$$\int \Phi(\mathbf{n}\,\delta\mathbf{D})\, dS = 0. \tag{8.29b}$$

Since $\delta\mathbf{D}$ is arbitrary except for the conditions (8.28*c*), it follows that (8.29*b*) requires that Φ be constant on the surface of any of the conductors,

$$\Phi = \Phi_k = \text{const (on } k). \tag{8.29c}$$

Hence the electrostatic field is a field distribution corresponding to a stationary value of the field energy.

To see that it is an absolute minimum we consider the second order variation of U which, on consulting (8.28) and (8.28*a*), is

$$\frac{1}{8\pi}\int \delta\mathbf{E}\,\delta\mathbf{D}\, d\tau = \int \varepsilon(\delta\mathbf{E})^2\, d\tau \tag{8.30}$$

for the electrostatic field. This variation is essentially positive for any variation of the field and proves that the electrostatic field energy is an absolute minimum for the system of charged conductors and an arbitrary dielectric.

9. CAPACITY (CAPACITANCE) OF A CONDENSER (CAPACITOR). CHARGE DISTRIBUTION ON CONDENSERS

Systems of Condensers

A condenser is a device used to collect electric charges on the surface of a conductor. In principle an elementary condenser consists of a primary conductor of any shape or size and a secondary conductor capable of saturating electric lines of force from the charges of the first one by equal charges of opposite sign when kept to a given potential. This potential is usually taken to be the earth's potential as conventionally given the value zero. The zero potential conductor may be an infinitely distant sphere or an infinitely distant plane (the earth's surface) or some closed surface of the secondary conductor enclosing the primary conductor and collecting the charge of opposite sign. The capacity of a single conductor is the amount of charge that raises its potential by one unit; its potential coefficient is the inverse, that is, the potential produced when it collects one unit of charge.

A system of condensers is a number of primary conductors supplemented by some common zero potential conductor like an infinitely distant sphere, the earth's surface, or some surrounding metallic surface of finite dimensions. (See Figs. 1-23*a* and 1-23*b*.)

The Plate, Sphere, and Cylinder Condensers

A plate condenser consists of two metallic plates placed side by side at a small distance d in comparison with the linear dimensions or the area S of

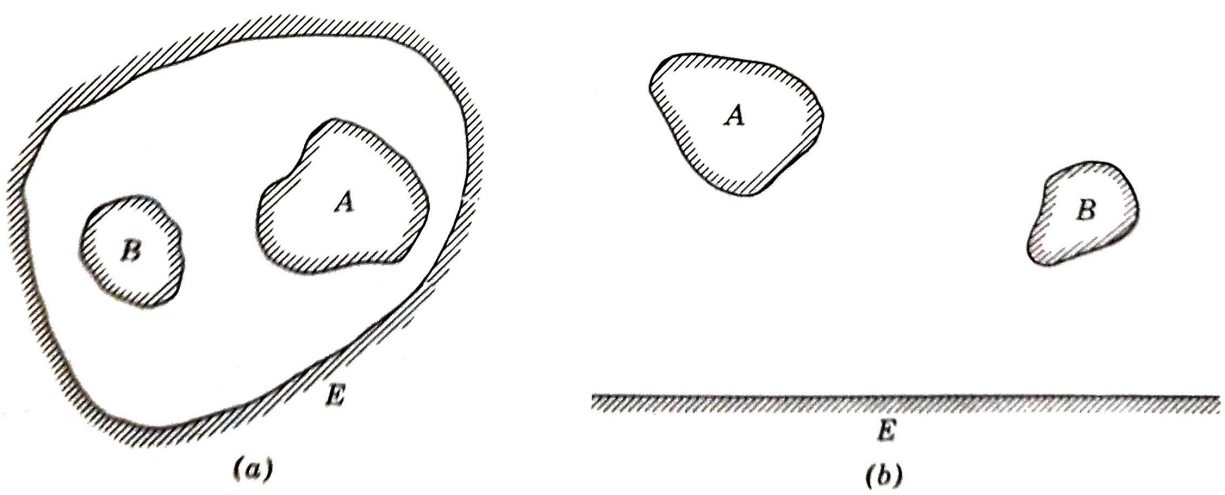

Fig. 1-23. (*a*) The principal feature of a condenser consisting of conductors A, B, . . . , surrounded by a conducting surface (*b*) A condenser with the earth representing the outer surface. A plane surface is the limiting case providing for saturation of field lines from A and B.

the plates, in order to insure an almost ideal homogeneous field between the plates. (See Fig. 1-24.) The one plate is grounded and the other takes the potential $\Phi = Ed$ with E the electric field strength. The charge on the plate becomes

$$e = \sigma S = \frac{\varepsilon E}{4\pi} S = \frac{\varepsilon \Phi}{4\pi d} S. \tag{9.1}$$

Hence the capacity is

$$C = \frac{\varepsilon}{4\pi d} S. \tag{9.2}$$

Since d is easily changed, the capacity of the plate condenser is easily varied. Plate condensers are also easily constructed for variation of effective plate areas by sideways displacement of the plates.

The sphere condenser consists of an inner metallic sphere or spherical surface and an outer one of zero potential. (See Fig. 1-25.) If the radii are a and b, respectively, the potential difference for a given inner charge e is

$$\Phi = \frac{1}{\varepsilon}\left(\frac{e}{a} - \frac{e}{b}\right) \tag{9.3}$$

and the capacity becomes

$$C = \frac{\varepsilon a b}{b - a}. \tag{9.3a}$$

In vacuum, $\varepsilon = 1$, and for an infinitely distant outer sphere we have $C = a$. The capacity therefore has the dimension of length, which in the electrostatic system is measured in centimeters.

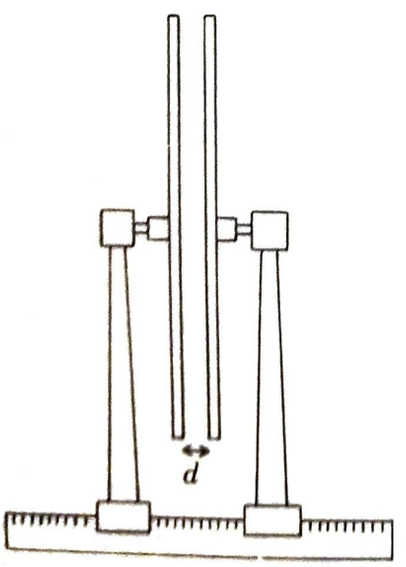

Fig. 1-24. The plate condenser.

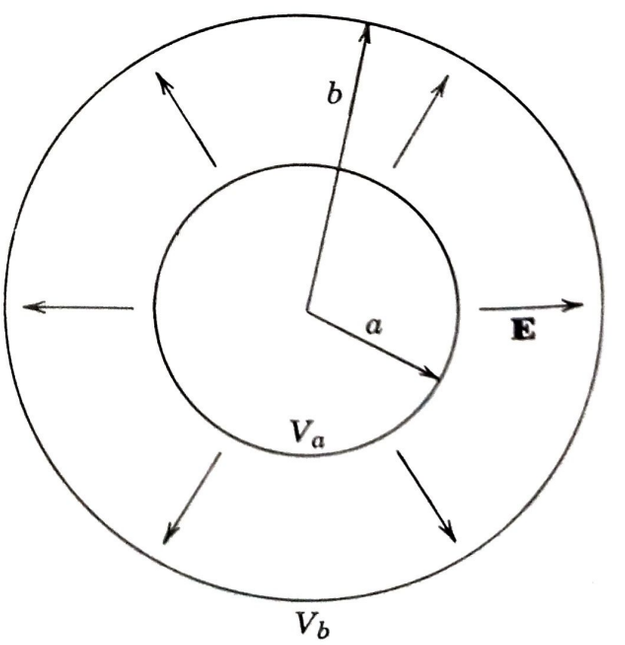

Fig. 1-25. The spherical condenser.

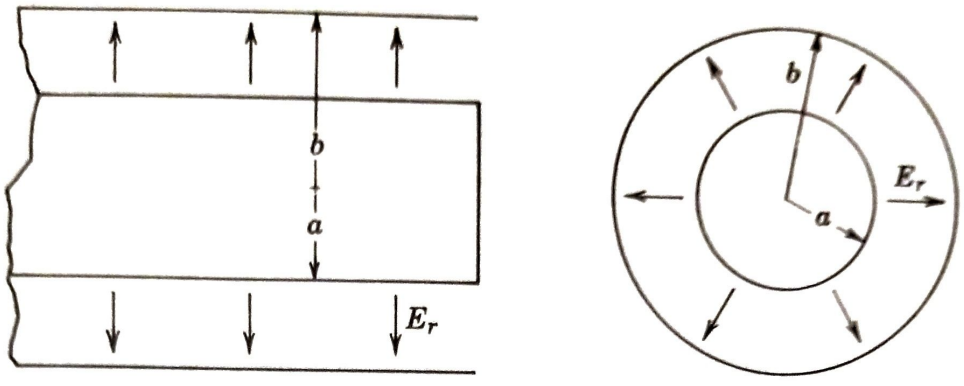

Fig. 1-26. The cylinder condenser.

The cylinder condenser consists of an inner and an outer grounded cylinder, both of them frequently of considerable length in comparison to their diameters. (See Fig. 1-26.) Its capacity per unit length is a zero-dimensional quantity and is found as follows.

If e is the charge per unit length, we have from the Gauss theorem

$$2\pi r\, D_r = 4\pi e \tag{9.4}$$

or

$$E_r = \frac{2e}{\varepsilon}\frac{1}{r}, \tag{9.4a}$$

and the potential difference for cylinder radii a and b becomes

$$\Phi = \frac{2e}{\varepsilon}\int_a^b \frac{dr}{r} = \frac{2e}{\varepsilon}\log\frac{b}{a}. \tag{9.4b}$$

Hence the capacity per unit length of a cylinder condenser is

$$C = \frac{\varepsilon}{2\log(b/a)}. \tag{9.5}$$

Capacity and Potential Coefficients of a System of Condensers

The potential energy of a number of charged conductors forming a condenser system is

$$U = \frac{1}{2}\sum_i e_i\Phi_i. \tag{9.6}$$

The charges are linear functions of the potentials, and vice versa,

$$e_i = \sum_k C_{ik}\Phi_k, \tag{9.6a}$$

$$\Phi_i = \sum_k p_{ik}e_k. \tag{9.6b}$$

The coefficients C_{ik} and p_{ik} are called capacity and potential coefficients, respectively, and are both of them symmetric,

$$C_{ki} = C_{ik}, \qquad p_{ki} = p_{ik}. \tag{9.6c}$$

They are, however, fairly complex quantities depending not only on the shape and position of a conductor pair i, k, but even on the shape and position of any of the conductors of the ensemble.

In principle the coefficients may be found as follows. If there are different dielectrics in the arrangement, we may replace discontinuities by layers of rapidly changing dielectric constant. Hence in general it suffices to replace the Laplace equation by

$$\operatorname{div}(\varepsilon\nabla\Phi) = 0. \tag{9.7}$$

We now look for a solution Φ_k of this equation having zero values for all conductors, except the one conductor k for which it has constant value. This solution we may normalize so that, in particular, its constant value on k becomes unity. On any of the conductors, say i, the corresponding total charge is found by taking the normal integral of the vector **D**; this obviously gives the capacity coefficient C_{ik}

$$C_{ik} = -\frac{1}{4\pi}\int \varepsilon \frac{\partial\Phi_k}{\partial n_i}\, dS_i. \tag{9.8}$$

Adding up similar solutions for the other conductors k multiplied by arbitrary constants in order to make Φ_k numerically an arbitrary solution, the result for the total charge e_i on the conductor i is seen to be given by (9.6*a*).

Similarly, if for boundary conditions we require the normal integral of **D** in (9.8) to be zero on all conductors apart from k which means no charges except on k, we may normalize this solution so that

$$-\frac{1}{4\pi}\int \varepsilon \frac{\partial\Phi_k}{\partial n_k}\, dS_k = 1. \tag{9.9}$$

This potential then takes the values p_{ik} on the conductors. On multiplying each solution by e_k and adding, the result is (9.6*b*).

The next step to prove that the coefficients C_{ik} or p_{ik} are symmetric is simple. On varying the charges infinitesimally we have

$$\delta U = \frac{1}{2} \sum_i (\delta e_i U_i + e_i \, \delta U_i). \tag{9.10}$$

On the other hand, we have from ordinary energy considerations

$$\delta U = \sum_i \delta e_i U_i \tag{9.10a}$$

whence

$$\sum_i \delta e_i \Phi_i = \sum_i e_i \, \delta \Phi_i. \tag{9.11}$$

Inserting e_i and δe_i from (9.6*a*) or Φ_i and $\delta \Phi_i$ from (9.6*b*), we obtain (9.6*c*).

Absolute Measurements. The Electricity Balance

Electrometers for measuring static electric charges, or rather potential differences or voltage, are devices based on the condenser principle with some movable part of the condenser causing variations of its capacity coefficients. In principle the measurements may be either absolute or relative.

The Kelvin absolute electricity balance, as shown in Fig. 1-27, is an instrument of the first kind. It may be taken to be a simple plate condenser with one movable plate connected with one arm of a sensitive balance kept in equilibrium by a weight on the other. Provisions are made for ensuring an ideal homogeneous field in the condenser gap. For instance, if the condenser plates are circular, the movable plate may be only an inner circular plate leaving an outer rigid circular ring for reducing irregularities at the edge of the plate.

Using the above notations for the plate area and plate distance, and so forth, we have the equilibrium condition

$$mg = \frac{1}{2} E \sigma S = \frac{\varepsilon}{8\pi} \frac{\Phi^2}{d^2} S, \tag{9.12}$$

with $\Phi = Ed$, from which we find the potential square

$$\Phi^2 = \frac{8\pi d^2}{\varepsilon S} mg. \tag{9.12a}$$

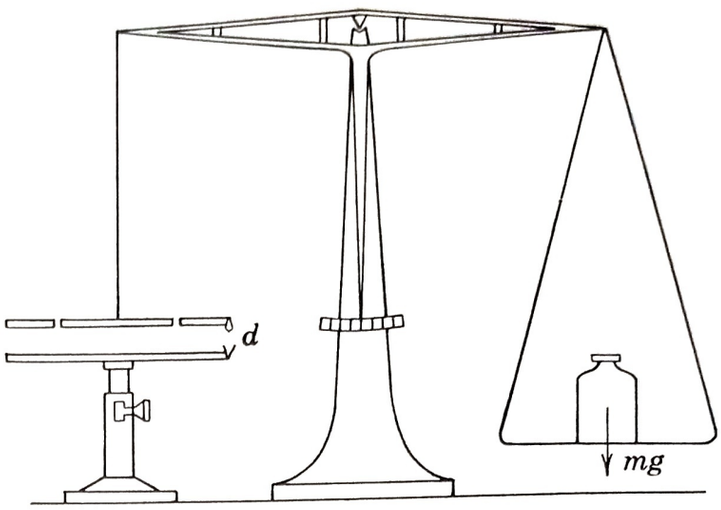

Fig. 1-27. The Kelvin electricity balance.

Hence the unit for voltage square is force, that is, in the Gaussian system, one dyne.

Relative Measurements. The Quadrant Electrometer

Another well-known measuring instrument also invented by Lord Kelvin is the quadrant electrometer. (See Fig. 1-28.) Although it is not an absolute instrument like the electricity balance, it is noted for its high sensitivity. Its main parts are a flat circular box split into four quadrants, with opposite quadrants in metallic connection, and an inside movable needle (or rather plate) suspended in a torsion wire which normally keeps the needle in a symmetric position with respect to the quadrants.

The shape of the needle increases its area inside a quadrant pair proportional to the rotational angle α as measured from the central position. By means of the torsion wire the needle is kept at a given potential Φ_3, whereas the potentials of the two quadrant pairs are Φ_1 and Φ_2.

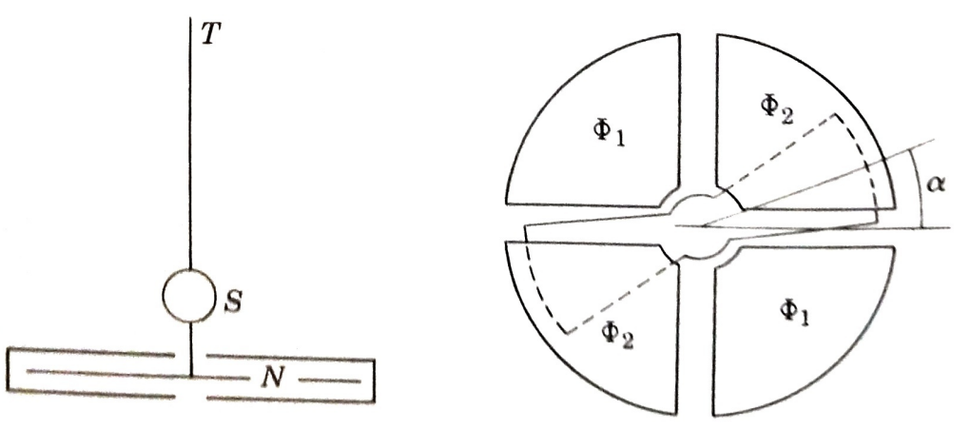

Fig. 1-28. The Kelvin quadrant electrometer.

From a practical point of view the quadrant electrometer problem is fairly simple. If studied in more detail, it provides some interesting theoretical aspects.

If the various conductors of a condenser system are provided with given charges, in the energetic sense a closed system is formed. Therefore the work done by the movable parts is taken from the field energy:

$$dW = -dU. \tag{9.13}$$

This is the principle used to demonstrate the field energy produced by mechanical forces on the plate condenser. Its energy is, as we have seen,

$$U = \frac{1}{2} e\Phi = \frac{1}{2} C\Phi^2 = \frac{1}{2C} e^2 \tag{9.13a}$$

with $C = \varepsilon S/4\pi d$ as given in (9.2).

On changing the distance at constant charge

$$\delta U = -\frac{e^2}{2C^2} \delta C = -\frac{1}{2} \Phi^2 \, dC, \tag{9.13b}$$

whereas at constant potential we have

$$\delta U = \tfrac{1}{2}\Phi^2 \, dC = \tfrac{1}{2}\Phi \, de. \tag{9.13c}$$

In the latter case, obviously, energy has been transferred to the system by outside forces to the amount of double the increase of field energy

$$\Phi \, de = 2\delta U = \delta U + \delta U, \tag{9.13d}$$

the one half being spent on the field energy and the other half on the work performed.

The general validity of the principle is easily seen by the following reasoning. With given potentials Φ_k on the conductors the increase of the potential energy, and hence also of the field energy, is

$$\delta U = \frac{1}{2} \sum_k \Phi_k \, de_k, \tag{9.14}$$

whereas the energy transferred to the system by providing the conductors with charges de_k is

$$\sum_k \Phi_k \, de_k = 2 \, \delta U. \tag{9.14a}$$

Hence the amount $2\delta U - \delta U = \delta U$ has been consumed by work.

The simple way of treating the quadrant electrometer is to consider only

variations of the capacity coefficients rather than the coefficients themselves. Since the electrometer quadrants form a practically complete shielding of the needle, the variation of charges obeys the law

$$\delta e_1 + \delta e_2 + \delta e_3 = 0. \tag{9.15}$$

Hence the corresponding variation of the potential energy or field energy of the system becomes

$$\begin{aligned} \delta U &= \tfrac{1}{2}(\Phi_1\,\delta e_1 + \Phi_2\,\delta e_2 + \Phi_3\,\delta e_3) \\ &= \tfrac{1}{2}[(\Phi_1 - \Phi_3)\,\delta e_1 + (\Phi_2 - \Phi_3)\,\delta e_2]. \end{aligned} \tag{9.15a}$$

Now

$$\delta e_1 = (\Phi_1 - \Phi_3)\,\delta C_{13}, \qquad \delta e_2 = (\Phi_2 - \Phi_3)\,\delta C_{23} \tag{9.15b}$$

and

$$\delta C_{23} = -\delta C_{13} = k\,d\alpha \tag{9.15c}$$

if the deviation angle α is counted in the direction of the quadrant pair 2. Here k is a proportionality factor depending on the size of the needle and its vertical distance from the base and the roof of the quadrant box. Hence

$$\delta U = \tfrac{1}{2}k\,\delta\alpha[(\Phi_2 - \Phi_3)^2 - (\Phi_1 - \Phi_3)^2]. \tag{9.16}$$

On the other hand, the energy variation of the torsion wire is

$$dW = \tau\alpha\,d\alpha, \tag{9.16a}$$

where $\tau\alpha$ is the torque on the wire proportional to the deviation angle α. Equating (9.16) and (9.16*a*), we obtain the result:

$$\alpha = \frac{k}{2\tau}[(\Phi_2 - \Phi_3)^2 - (\Phi_1 - \Phi_3)^2]. \tag{9.17}$$

The electrometer may be used mainly in two different ways. Connecting the needle with the quadrant 1, $\Phi_1 = \Phi_3$, the so-called idiostatic coupling, we obtain the result

$$\alpha = \frac{k}{2\tau}(\Phi_2 - \Phi_1)^2, \tag{9.17a}$$

and the instrument may be used even for measurements of alternating potentials.

The other way of coupling is called heterostatic. The needle is connected to a very high potential Φ_3, so that in the resulting formula

$$\alpha = \frac{k}{\tau}(\Phi_1 - \Phi_2)\left[\Phi_3 - \frac{1}{2}(\Phi_1 + \Phi_2)\right] \tag{9.17b}$$

we may neglect the last term in the bracket and simply take $\Phi_1 - \Phi_2$ proportional to the deviation angle.

In both cases we have a square or product voltage measured by a mechanical force.

10. MAGNETOSTATICS

Preliminaries

Observations of magnetic phenomena probably are as old as those of electricity. In the mineral Fe_3O_4 (magnetite) nature presents us with a material of strong magnetic properties. The name magnetite, as well as magnetism for its properties, is derived from its place of discovery or, maybe, its first place of abundance: Magnesia in Asia Minor. The first man to make thorough systematic studies of magnets and magnetism was, however, William Guilbert.

A magnet usually consists of a piece of iron, steel, nickel, or other substances which by some means or other have been magnetized and are able to remain in that state of permanent magnetism. Such magnets attract pieces of iron and other magnetizable substances. Next a magnetized rod or needle suspended so as to be free to rotate horizontally, or floating on some piece of light material on a water surface, orients itself in a definite direction. It feels forces that man does not know, namely the magnetic field of the earth.

In studying magnetic forces it is found that they originate from some fairly concentrated spots on a permanent magnetic rod, called its magnetic poles. It is as though those poles possessed something similar to electric charges. The phenomena of electricity and magnetism are similar also in that there apparently are two kinds of electric and magnetic substances (or fluids) capable of neutralizing each other: positive and negative electricity; and positive and negative magnetism. The corresponding names of north and south pole magnetism present themselves for natural reasons, the north pole of a magnet being that which points to the north in the natural magnetic field of the earth.

There is a characteristic difference, however, of the greatest importance: the two kinds of magnetism can never be fully separated. You cannot take away the positive or the negative magnetism as you can do with positive and negative electric charges. Wherever positive magnetism appears it is followed by an equal amount of negative magnetism somewhere in the neighborhood. The smallest magnetic element is not a magnetic charge; it is a magnetic dipole corresponding to the electric dipole in the pure mathematical sense.

How the apparent separation of magnetic charges to either end of a magnetic rod is effected is illustrated in any school book on physics. Mathematically we may look upon it in exactly the same way as when considering a piece of dielectric in the state of polarization. For even polarization there

are no electric charges inside the piece of matter, although there are some faint free charges by uneven polarization. Free charges in some abundance appear only on the surface and, in particular, where the polarization is normal to the surface.

The Coulomb Law for Magnetic Forces

According to the above view a long and thin and evenly magnetized rod will present us with two concentrated spots of free magnetism at the end points of the rod. If we were allowed to adopt the concept of magnetic charges, those charges would be equal in size and opposite in sign.

Moreover, idealizing the picture by considering an extremely long rod we would be close to having realized a single magnetic charge at both the end points.

For two such charges, say, m_1 and m_2, we might be able to measure their interacting force and express them by some law of force

$$F = m_1 m_2 f(r). \tag{10.1}$$

Next we might use the law for defining a unit of magnetic charge in the same way as in electrostatics, namely, by stating that for unit charges $m_1 = 1$, $m_2 = 1$ the force F at distance $r = 1$ should be unity in the adopted system of fundamental mechanical units. If it proves possible to put $f(r)$ in the definite form

$$f(r) = \frac{1}{r^2}, \tag{10.2}$$

then we have the Coulomb law for magnetism.

We need not do it just in that way, however, because the Coulomb law is the basis for the field of force or the potential of an electric dipole to the same degree as it is the basis for the potential of a point charge. Hence we may as well start with the concept of the field from a magnetic dipole. Since we are using the letter m for magnetic charges, we may now adopt it for the more realistic concept of a magnetic dipole corresponding to p for an electric dipole in electrostatics. Hence the elementary magnetic potential becomes

$$\Phi_m = \frac{\mathbf{mr}}{r^3} \tag{10.3}$$

and the corresponding magnetic field of force is

$$\mathbf{H} = -\nabla\Phi_m = -\frac{\mathbf{m}}{r^3} + 3\frac{(\mathbf{mr})\mathbf{r}}{r^5}. \tag{10.4}$$

At the same distance in the direction of the dipole and perpendicular directions, the field strengths are in a proportion 2:1 and the field direction

parallel and antiparallel to the dipole, respectively. The resulting torques on a magnetic needle on these spots can be measured by means of the magnetic field of the earth by placing the magnetic dipole perpendicular to the field. In principle this is crucial for verification of the Coulomb law of magnetostatics.

Measurements of Magnetic Moments and Field Strengths

For convenience we use the abbreviation magnetic moment for the magnetic dipole moment. It can be measured against an external magnetic field like the approximately homogeneous field $\mathbf{H}_0$ of the earth. The two previously mentioned positions of a testing magnetic needle are called the Gauss principal positions. (See Fig. 1-29.) In the first case the magnetic field strength at $r = r_0$ is $H = 2m/r_0^3$, so that by a deviation α of the magnetic needle from the direction of the earth's field we have

$$\tan \alpha = \frac{H}{H_0} = \frac{2m}{H_0 r_0^3}. \tag{10.5}$$

On the other hand, the magnetic rod as represented by the dipole m may be suspended so as to be able to perform free oscillations to either side of the direction of the earth's field. If α is again the angle of deviation, we have

$$I \frac{d^2\alpha}{dt^2} = -mH_0 \sin \alpha, \tag{10.6}$$

where for small oscillations we have a definite measurable frequency

$$\omega = \sqrt{\frac{mH_0}{I}}, \tag{10.6a}$$

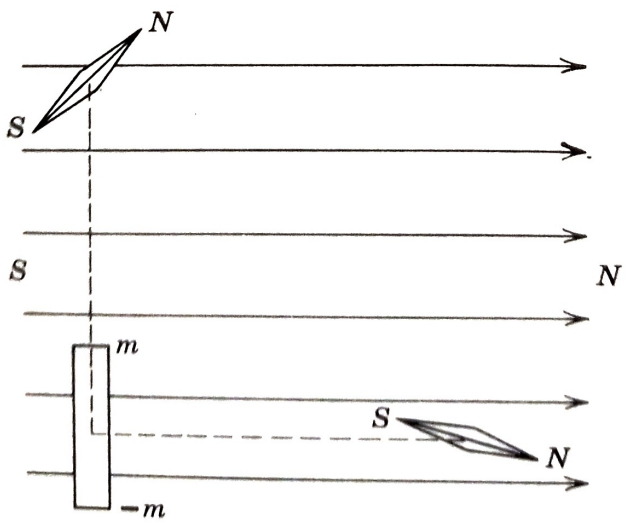

Fig. 1-29. Measurement of magnetic field strengths in Gauss' main positions versus the earth's magnetic field.

or

$$mH_0 = I\omega^2, \tag{10.6b}$$

where again the moment of inertia is a measurable quantity.

Hence the two fundamental measurements determine the ratio as well as the product of m and H_0. It is seen that the dimensions of m and H_0 are the same as for p and E in electrostatics, namely, magnetic moment = magnetic field strength times volume, and mH_0 = mechanical torque.

Analogies with Electrostatics

According to the above view a magnetic field of force originates from magnetized pieces of matter. If the density of the magnetic moment is denoted by **M**—corresponding to the dielectric polarization **P**—then from the elementary law (10.3) the magnetic potential is

$$\Phi_m = \int \frac{\mathbf{Mr}}{r^3}\, d\tau \tag{10.7}$$

with the magnetic field

$$\mathbf{H} = -\nabla\Phi_m. \tag{10.7a}$$

The integral (10.7) may be transformed into

$$\Phi_m = \int \left[\operatorname{div}\left(\frac{\mathbf{M}}{r}\right) - \frac{\operatorname{div}\mathbf{M}}{r} \right] d\tau \tag{10.7b}$$

indicating a free magnetic charge density

$$\rho_m = -\operatorname{div}\mathbf{M} \tag{10.7c}$$

according to the Coulomb law. Correspondingly transforming the first integral in (10.7*b*) by use of the Gauss integral theorem into a surface integral, we obtain formally a surface density of magnetic charges acting according to the Coulomb law.

Now consider a small region inside a piece of magnetized matter and calculate there the divergence of the magnetic field. The first term in (10.7*b*) then is obviously insignificant, since it can be referred to as originating from outside charges, that is, on the surface of the magnetized body. It remains to consider only the last term of (10.7*c*) where the integrand can be replaced by ρ_m/r. From corresponding equations of electrostatics it follows that

$$\operatorname{div}\mathbf{H} = 4\pi\rho_m \tag{10.8}$$

and hence, on introducing the vector

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}, \tag{10.9}$$

we have

$$\operatorname{div}\mathbf{B} = 0. \tag{10.9a}$$

The vector **B** is called the magnetic induction and replaces the dielectric displacement—or simply displacement vector—**D** in electrostatics. Since there is no true magnetic charge density equivalent to the charge density ρ of electrostatics it is quite natural that

$$\text{div } \mathbf{D} = 4\pi\rho \tag{10.9b}$$

should be replaced by (10.9*a*) in magnetostatics.

Magnetic Properties of Matter

Writing

$$\mathbf{M} = \kappa_m \mathbf{H}, \qquad \mathbf{B} = \mu \mathbf{H}, \qquad \mu = 1 + 4\pi\kappa_m, \tag{10.10}$$

κ_m is the magnetic susceptibility and μ the permeability, the latter corresponding to the dielectric constant ε. Whereas in electrostatics $\varepsilon \geqq 1$, the permeability μ may be both smaller and larger than unity. In the first case of negative κ_m the substance is called diamagnetic, in the latter case paramagnetic.

In both cases we assume field-independent material constants. However, in substances like soft iron these constants depend to a great extent on the field strength, being on the whole of an extraordinarily large order of magnitude and ending up at some sort of saturation of the magnetization. These are the ferromagnetic substances.

Finally we have the phenomena of magnetic hysteresis and permanent magnetism, the latter requiring a formula for magnetization of the form

$$\mathbf{M} = \kappa_m \mathbf{H} + \mathbf{M}_0 \tag{10.11}$$

with $\mathbf{M}_0$ representing the permanent magnetization.

We cannot here enter into the difficult theories of permanent magnetism nor even of ferromagnetism. The simplest theory is that of diamagnetism which may be thought of as resulting from atomic circular currents set up by the applied magnetic field. The negative sign of the magnetization or the susceptibility is then in accordance with well-known principles of nature.

The paramagnetism, on the other hand, is caused by existing real magnetic dipoles in the substance in the form of, say, molecules with permanent magnetic moments. When in the state of molecular disorder the molecules produce no macroscopic magnetization. In a magnetic field, however, they become partly orientated in the direction of the field, and their magnetic momenta add up to a macroscopic magnetization of the substance. This ordering of the molecules must however compete with the disordering process of thermal agitation. The paramagnetism therefore becomes dependent on temperature and of course decreases with rising temperature so that under given circumstances the usually fainter diamagnetism may compete and subdue the paramagnetism.

The dependence of paramagnetism on temperature, moreover, is not of a simple kind, particularly not at low temperatures. In that region a particular theory is needed in which the so-called Curie law and Curie temperature play an important role. We shall not discuss this theory in the present description of magnetic phenomena.

It should be mentioned, however, that the interaction of a magnetic field with the eigenspin of the free electrons in metals produces paramagnetism, which even to some extent is easily accounted for numerically.

We may, however, recall the elementary definition of magnetic field strength and induction inside a magnetized body as given by Lord Kelvin. If a cavity is carved inside a magnetic body, free magnetic charges will appear on its boundaries. If the cavity is a long narrow tunnel, the effect of the charges at the ends have only minute effects and the field can be defined as **H**. (See Fig. 1-30.)

If the cavity has the form of a very low pill-box placed perpendicular to the field, there will be surface charges $-M_n$ and M_n at the front and rear of the cavity, respectively, so that the effective field becomes

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} \tag{10.12}$$

which is the induction vector according to (10.9).

Field Energy and Stress Tensor of the Magnetic Field

Consider two independent and movable permanent magnets, say, in the form of long and evenly magnetized rods and for idealizations with equal and opposite constant densities of free magnetic charge σ_m and $-\sigma_m$ at their end surfaces. If we also imagine the surfaces to be of equal size and not too small, they may be placed together to form a narrow slit representing a double magnetic layer.

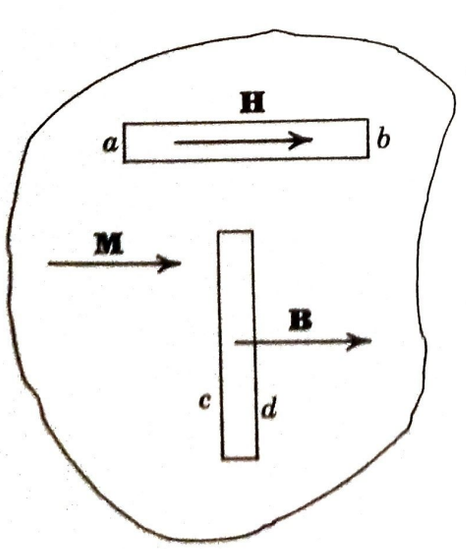

Fig. 1-30. Kelvin's definition of **H** and **B** by means of cavities in a magnetic body.

The normal component of the field is $H_n = 4\pi\sigma_m$, so that the stress per unit area is

$$f_n = \frac{1}{2}\sigma_m H_n = \frac{1}{8\pi}\mathbf{H}^2. \tag{10.13}$$

Starting with the magnetic surfaces in close contact and separating them to a distance d, we have to apply a force $F = f_n S$, where S is the area of the surface. The work done by separation then is the expression (10.13) multiplied by the volume Sd between the end surfaces. If the field is thought of as produced by that mechanical work, the expression (10.13) again represents the field energy density.

When studying the same field in a magnetic body, for simplicity a gas or a fluid with permeability μ, we have to remember that the magnetic field is reduced in proportion $1/\mu$, that is,

$$H_n = \frac{4\pi\sigma_m}{\mu}, \qquad B_n = \mu H_n = 4\pi\sigma_m. \tag{10.14}$$

Equation 10.13 is therefore changed into

$$f_n = \frac{1}{2}\sigma_m H_n = \frac{1}{8\pi}\mathbf{BH}, \tag{10.14a}$$

and we have a field energy density

$$u_m = \frac{1}{8\pi}\mathbf{BH} \tag{10.15}$$

in perfect analogy with the energy density in an electric field.

The analogy persists in the formula for mechanical forces acting upon magnetic bodies in the presence of a magnetic field

$$\mathbf{F}_m = -\frac{1}{8\pi}\mathbf{H}^2\nabla\mu = \frac{1}{8\pi}(2\mathbf{H}\,\mathrm{div}\,\mathbf{B} - \mathbf{H}^2\nabla\mu), \tag{10.16}$$

where in the last expression the zero term with div **B** has been added for the sake of comparison with the electrostatic field. It follows that there will be a Maxwell magnetic stress tensor

$$T_m = \frac{1}{8\pi}(2\mathbf{B}\cdot\mathbf{H} - I\mathbf{BH}) \tag{10.17}$$

corresponding to the tensor (8.23a) for the electrostatic field. The tensor represents surface forces acting from any part of a magnetic body to neighboring parts through fictitious dividing surfaces.

The Vector Potential

The general characteristics of the magnetic field vector in magnetostatics are

$$\operatorname{curl} \mathbf{H} = 0 \tag{10.18}$$

corresponding to its possible representation by a magnetic potential

$$\mathbf{H} = -\nabla \Phi_m. \tag{10.18a}$$

The general characteristics of the induction vector, on the other hand, are

$$\operatorname{div} \mathbf{B} = 0. \tag{10.19}$$

This renders it possible to represent the induction vector **B** by a vector potential **A** in the form

$$\mathbf{B} = \operatorname{curl} \mathbf{A}. \tag{10.19a}$$

In virtue of the relation $\mathbf{B} = \mu\mathbf{H}$ there is no essential difference between **B** and **H** in a medium of constant μ. In such a medium both vectors are Laplacian and are expressible in either way by a scalar potential and a vector potential, the only difference being the factor μ. The essential difference first appears in the region of the sources of the field which are now considered to be closed circular electric currents of either macroscopic or molecular origin.

In electrostatics we are familiar with the elementary potential $1/r$ of a unit charge, as well as with its electric field vector $\mathbf{r}/r^3$. Outside of its singularity in $r = 0$ the field vector is a Laplacian vector, that is, with zero divergence and curl. It may be useful to know that the same is true for any vector

$$\mathbf{b} = \frac{\mathbf{s} \times \mathbf{r}}{r^3}, \tag{10.20}$$

with **s** a given arbitrary vector, because of

$$\operatorname{div} \mathbf{b} = -\mathbf{s} \operatorname{curl} \frac{\mathbf{r}}{r^3} \tag{10.20a}$$

and

$$\operatorname{curl} \mathbf{b} = \mathbf{s} \operatorname{div} \frac{\mathbf{r}}{r^3}. \tag{10.20b}$$

We may also write

$$\mathbf{b} = \operatorname{curl} \frac{\mathbf{s}}{r} \tag{10.21}$$

and this suggests the use of

$$\mathbf{a} = \frac{\mathbf{s}}{r} \tag{10.21a}$$

as an elementary part of the vector potential **A**. Writing, for instance, **A** in the form of a closed curve integral

$$\mathbf{A} = M\oint \frac{d\mathbf{s}}{r}, \tag{10.22}$$

it is found that

$$\operatorname{div}\mathbf{A} = -M\oint \frac{\mathbf{r}\,d\mathbf{s}}{r^3} \tag{10.22a}$$

when referring the differentiation to a field point P in space. On integrating, however, the variable is the source point Q with $d\mathbf{s} = -d\mathbf{r}$. Hence we have

$$\operatorname{div}\mathbf{A} = M\oint \frac{dr}{r^2} = -M\oint d\left(\frac{1}{r}\right). \tag{10.22b}$$

If therefore $d\mathbf{s}$ is the vectorial line element of a closed curve, the integral (10.22*b*) is zero and **A** becomes a divergence-free vector.

Now for a moment we return to our divergence-free induction vector **B** of (10.19*a*). According to general rules this vector is uniquely determined by its curl for which we write

$$\operatorname{curl}\mathbf{B} = 4\pi\mathbf{m}. \tag{10.23}$$

For its vector potential we may conveniently require the permissible restriction

$$\operatorname{div}\mathbf{A} = 0 \tag{10.23a}$$

which on account of

$$\operatorname{curl}\operatorname{curl}\mathbf{A} = \nabla\operatorname{div}\mathbf{A} - \nabla^2\mathbf{A} \tag{10.23b}$$

leads to the vectorial Poisson equation

$$\nabla^2\mathbf{A} = -4\pi\mathbf{m} \tag{10.23c}$$

with the solution

$$\mathbf{A} = \int \frac{\mathbf{m}}{r}\,d\tau. \tag{10.24}$$

From (10.23) we have $\operatorname{div}\mathbf{m} = 0$, which means that

$$\operatorname{div}_q\left(\frac{\mathbf{m}}{r}\right) = \mathbf{m}\nabla_q\left(\frac{1}{r}\right) = -\mathbf{m}\nabla_p\left(\frac{1}{r}\right) = -\operatorname{div}_p\left(\frac{\mathbf{m}}{r}\right) \tag{10.24a}$$

or

$$\operatorname{div}\mathbf{A} = -\int \operatorname{div}_q\left(\frac{\mathbf{m}}{r}\right)d\tau. \tag{10.24b}$$

By use of the Gauss integral theorem, (10.24*b*) can be transformed into a closed surface integral which, on taking the surface to be at infinite linear distances, becomes zero.

The vector **m**, being divergence-free or solenoidal, has vector lines ending at infinity or forming closed curves. Consider therefore a tube bounded by vector lines and with cross section q of possible variable size, the product

$$M = |\mathbf{m}|\, q \tag{10.24c}$$

must be constant owing to the solenoidal character of **m**. Next, for a very narrow tube with uniquely defined **m** we write

$$\mathbf{m}\, d\tau = \mathbf{m} q\, ds = M\, d\mathbf{s} \tag{10.24d}$$

with $|d\mathbf{s}| = ds$. The vector potential (10.24) transforms into the vector potential (10.22). In the latter case we call the closed curve of integration a rotational or vortex line of the vector field, whereas (10.24) with the above restrictions represents a field with, possibly, a very large number of vortex tubes of a certain rotational strength. It is fairly obvious that in field points far away from the vortices of the field it does not matter very much if we replace a tube vortex of moderate cross section by a line vortex. For that reason we shall study more closely the field of the vortex line, which from (10.19*a*) and (10.22) is

$$\mathbf{B} = \operatorname{curl} \mathbf{A} = M \oint d\mathbf{s} \times \frac{\mathbf{r}}{r^3}. \tag{10.25}$$

On taking **B** to be a potential gradient $\mathbf{B} = -V\Phi_m$ we start to find the potential Φ_m.

To that end we multiply **B** by $d\mathbf{r}$ to obtain

$$d\Phi_m = -\mathbf{B}\, d\mathbf{r} = M \oint \frac{\mathbf{r}}{r_3} (d\mathbf{s} \times d\mathbf{r}). \tag{10.26}$$

Now $d\mathbf{s} \times d\mathbf{r} = -d\mathbf{r} \times d\mathbf{s}$ is the vectorial surface element produced by a translation $-d\mathbf{r}$ of the line element $d\mathbf{s}$. Its scalar product with $\mathbf{r}/r^3$ is a solid angle $d\omega$ which, when integrated along the vortex line according to (10.26) still is an infinitesimal solid angle $d\Omega$. Hence

$$d\Phi_m = M\, d\Omega. \tag{10.26a}$$

Imagining the vortex line to be the boundary of a surface S, we find that the solid angle $d\Omega$ is obviously the difference of the solid angles subtended by the surface S as seen from the field points **r** and $\mathbf{r} + d\mathbf{r}$, since in this respect a translation $d\mathbf{r}$ of the field point is equivalent to the opposite translation $-d\mathbf{r}$ of the vortex line. Hence we may write

$$\Phi_m = M\omega \tag{10.27}$$

with ω the solid angle subtended by the surface S or its boundary curve, provided that we correctly define a positive side of the surface as uniquely

determined by the positive direction of its circumference. It is easily found that the correct definition corresponds to the well-known right-hand rule of coordinate systems.

The Equivalence of the Line Vortex and the Magnetic Double Layer

Consider the same surface S provided with a double magnetic layer of constant magnetic moment density M, or, as a vectorial density $\mathbf{M} = M\mathbf{n}$ with $\mathbf{n}$ the positive normal of S at the source point in question. The scalar magnetic potential

$$\Phi_m = \int \frac{\mathbf{Mr}}{r^3}\, dS = M \int \frac{\mathbf{r}\, d\mathbf{S}}{r^3} \tag{10.28}$$

is easily recognized as M times ω, the solid angle subtended by the positive side of S as seen from the field point. (See Fig. 1-31.)

Hence the postulated equivalence is proved. It remains only to state that, whereas the potential of the double layer is unique with a discontinuity in the double layer, there is no such discontinuity in the potential (10.27) for the vortex line where the surface S is only fictitious and with arbitrary form and position, except for its boundary curve.

The potential difference for opposite points on either side of the magnetic double layer is easily seen to be $4\pi M$. Hence we have for a closed line integral of $\mathbf{B}$ around the vortex line

$$\oint \mathbf{B}\, d\mathbf{r} = 4\pi M. \tag{10.29}$$

This also is a simple consequence of Stokes's theorem as applied to $\mathbf{B}$ and $\mathbf{A}$,

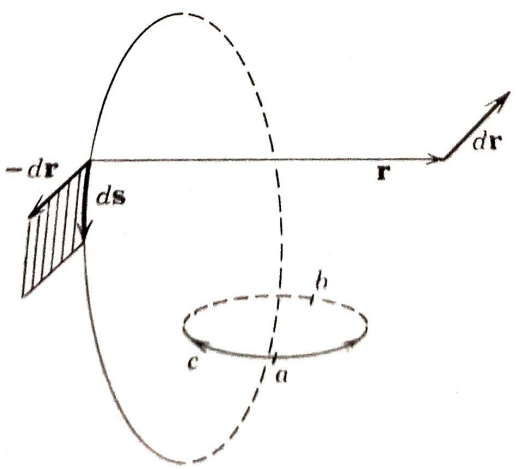

Fig. 1-31. For the explanation of the equivalence of the field of a magnetic double layer and the field of a vortex line corresponding to a current circuit around the border line of the layer.

namely, the equation

$$\oint \mathbf{B}\, d\mathbf{r} = \int \operatorname{curl} \mathbf{A}\, d\mathbf{f}, \tag{10.29a}$$

the latter integral giving the strength of the vortex which by (10.23) and (10.24*c*) is already defined as $4\pi M$.

Replacing M by J/c, J being the strength of an electric current in a closed conducting wire, we may term the above results the equivalence of a circular current and a magnetic double layer.

CHAPTER 2

Electromagnetism and Electrodynamics

11. STATIONARY ELECTRIC CURRENTS

Current Strength and Current Density

When movable electric charges are present in an electric field a transport of the charges called electric currents will be set up. The currents may be convective or conductive according to the mode of transport. In the convective currents the carriers of electric charges are charged atoms or molecules, that is, positive or negative ions. In conductive or metallic currents the carriers are electrons that are free or only loosely bound and therefore usually termed free electrons.

When two conductors of different potentials are connected by a metallic wire, an electric current begins to flow. To characterize the strength of the current we choose a positive direction of the wire and define the current strength—or simply current—by the equation

$$J = \frac{de}{dt}. \tag{11.1}$$

Here the meaning of de is the charge transported from the one conductor to the other in the time interval dt. The definition tells nothing about the sign of the charge of the carriers. For negative electrons in a metal their direction of motion is, of course, in the opposite direction of what is called the positive direction of the current.

In principle the current may vary from the one cross section to the other of the wire. In that case we have to define the current for individual cross sections, so that the quantity de has the meaning of an amount of electric charge passing the particular cross section. If the current varies, there will be an accumulation of charges in various parts of the wire. For a simple thin metallic wire this is, of course, a nonrelativistic view, but in conductors of arbitrary forms and dimensions it is the only correct general assumption.

For that reason we have to introduce a more accurate description by using the concept of current density which we denote by a vector $\mathbf{j}$. If $J = de/dt$ is

the current through a surface element $d\mathbf{S}$ of arbitrary orientation within the conductor, then the current density is defined by the equation

$$\mathbf{j}\, d\mathbf{S} = J. \tag{11.2}$$

The current J of course varies with the orientation of $d\mathbf{S}$ in such a way that $\mathbf{j}$ has the character of a vector. If the surface normal is in the direction of $\mathbf{j}$, that is, the surface element is normal to the direction of the current, we have

$$j\, dS = J \tag{11.2a}$$

for the magnitude j of the current density.

Conservation of Charge. Equation of Continuity

In the theory of electricity it is a fundamental assumption that a net sum of electric charges cannot be annihilated but only neutralized by an equal amount of charge of opposite sign. This view holds even in the now well-known case of actual annihilation of electron pairs (electron and positron with net charge sum zero). This is called the law of conservation of electric charge which is supported by all known experiments.

In a body with charge currents of density $\mathbf{j}$ consider a closed surface with surface elements $d\mathbf{S}$ as oriented according to the outside normal; the flow of electric charge through the surface is followed by a decrease of charge in the inside space. Referring the quantities to unit time, we have the equation

$$\int \mathbf{j}\, d\mathbf{S} = -\frac{de}{dt}. \tag{11.3}$$

On contracting the surface to an infinitesimal sphere around a field point in space we arrive at the differential equation

$$\operatorname{div} \mathbf{j} = -\frac{d\rho}{dt} \tag{11.4}$$

which is called the continuity equation for electric charges. It is valid for any transport of electric charges. If, however, we want the situation to be a stationary one, the right-hand side of (11.4) must be zero. Then charges are no more accumulating anywhere in the body (or bodies). We have a *stationary current* governed by the principal equation

$$\operatorname{div} \mathbf{j} = 0. \tag{11.5}$$

For practical purposes with respect to a network of conducting wires this may be expressed by the two Kirchhoff's laws for charge and for potential differences or voltages between branching points of the network.

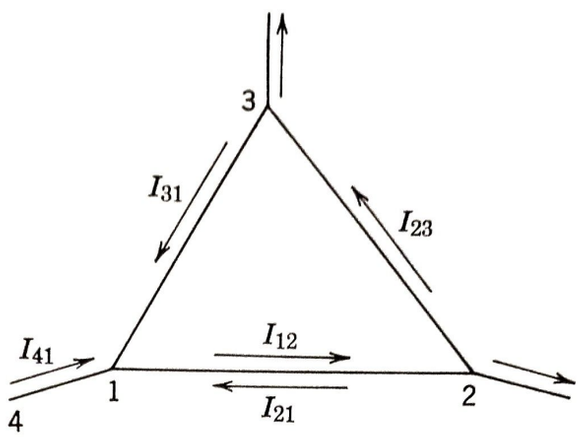

Fig. 2-1. Illustration of Kirchhoff's laws for conducting networks.

Let 1, 2, 3 be three such points forming a triangle of the network and let 41 be a wire leading from point 4 to point 1. We have

$$J_{41} + J_{21} + J_{31} = 0$$
$$\sum_k J_{kj} = 0 \tag{11.6}$$

for an arbitrary number of branches, and this is the Kirchhoff first law. Denoting the potential differences similarly, we obviously have

$$\Phi_{12} + \Phi_{23} + \Phi_{31} = 0. \tag{11.7}$$

According to Ohm's law this may be written

$$R_{12}J_{12} + R_{23}J_{23} + R_{31}J_{31} = 0, \tag{11.7a}$$

where the R's are the resistances of the wires.

Equation 11.7*a* is, however, only half true. Even in the case of stationary currents there are so far unexplained elements of the process: the so-called *electromotive* forces.

Electromotive forces may be of electromagnetic nature. They are also present in the form of galvanic elements as maintained by potential chemical reactions or thermoelectric forces maintained by thermal processes. In the theory of stationary currents electromotive forces of whatever origin are simply considered external forces capable of keeping definite potential differences between given points or cross sections of linear conductors. If such electromotive forces E_{12}, and so forth, are taken into account, (11.7*a*) is replaced by

$$R_{12}J_{12} + R_{23}J_{23} + R_{31}J_{31} = E_{12} + E_{23} + E_{31}; \tag{11.8}$$

this is the second Kirchhoff law which is easily generalized to any loop through a given network of conductors.

Ohm's and Joule's Laws

These are well-known laws from elementary physics which have been carefully verified by experiments for a great variety of material bodies. Their validity rests upon the correctness of the assumption

$$\mathbf{j} = \sigma \mathbf{E} \tag{11.9}$$

where σ is the *conductivity* of the material. The conductivity is considered independent of space coordinates within a homogeneous body and also independent of the strength of the electric field $\mathbf{E}$.

For a linear conductor of constant cross section q and length l in which a steady current is flowing, we then have $J = jq$ and the voltage $V = lE$. Hence from (11.9)

$$J = \sigma q E = \sigma \frac{q}{l} V. \tag{11.10}$$

Introducing $\rho = 1/\sigma$, the *resistivity* of the material, we have

$$V = RJ, \qquad R = \frac{\rho l}{q}; \tag{11.11}$$

this is Ohm's law. The *resistance* R is determined by the material constant ρ, and the shape and dimensions of the conductor. For linear conductors it is proportional to the length and inversely proportional to the cross section.

Per unit time an amount i of electricity has been transported through the potential difference V. According to the laws of electrostatics this means a loss of potential energy to the amount of VJ. From the law of conservation of energy the energy must reappear in some other form, which is here thermal energy. As there is no smoothing-out of potential differences in the picture of stationary currents the only permanent change is the appearance of thermal energy resulting in a heating of the conductor or its surrounding bodies. This energy obviously comes from the work done by outside or electromotive forces. If the conductors are cooled, the heat Q removed can be measured to verify the obvious result

$$Q = VJ = RJ^2; \tag{11.12}$$

this is Joule's law.

Elementary Electron Theory of Metals

To present a theory for conduction of electricity we must make some assumption as to the nature of carriers of electric charges. In the case of metallic conductors they are believed to be mainly or exclusively electrons in the state of free particles. This means that a certain number of the outer

electrons in a metallic atom, called conducting electrons, are no more tightly bound to the atoms but are moving collectively through space like the molecules of a gas. As in a molecular gas the motion is interrupted by colliding processes, maybe not so much by mutual collisions as by the capturing forces of the atoms which have been deprived of their natural balancing elements, their missing outer electrons.

To account for these interruptions we introduce the rough conception of a mean free path λ of the electrons so that, if the mean thermal velocity for the electrons is u, the time left for uninterrupted accelerations of the electrons in an electric field is

$$t = \frac{\lambda}{u}. \tag{11.13}$$

The distribution of thermal velocity is isotropic and does not contribute to any electric current. The current is due to an additional velocity v in the direction of the electric field. The acceleration in a field $\mathbf{E}$ is $a = eE/m$ with m the mass of the electron. At the end of each acceleration period the electron has acquired an additional electron velocity, so that its mean velocity during the interval of acceleration becomes

$$v = \frac{1}{2} at = \frac{e\lambda}{2mu} E. \tag{11.13a}$$

Multiplying by the charge ne of n free electrons per unit volume, the current density is

$$\mathbf{j} = \frac{ne^2\lambda}{2mu} \mathbf{E}, \tag{11.14}$$

from which we obtain the conductivity

$$\sigma = \frac{ne^2\lambda}{2mu}. \tag{11.14a}$$

This makes the conductivity depend on temperature in accordance with experimental findings. However, since the absolute temperature of an ideal gas is proportional to the mean kinetic energy $\frac{1}{2}mv^2$ of its moving particles, the expected temperature dependence of σ should be a proportionality to $T^{-1/2}$. For low temperatures the experience points rather to a proportionality with T^{-1} and does not support the above theory very much. However, we are now already involved in statistical laws and interpretations which must be left for finer statistical theories, including quantum statistics. For the sake of comparison and to obtain support from experience in other fields we therefore turn to the problem of heat conduction, using the same elementary conceptions and considerations.

Consider a metallic body with a temperature gradient ∇T or $\partial T/\partial x$ if taken in the x-direction. This means that the mean thermal velocity u of the electrons varies with x. If there are n electrons per unit volume, we will take the rough view that $\frac{1}{6}$ of them are moving in the positive x-direction. Hence $\frac{1}{6}nu$ electrons will pass per unit time and unit area through a surface perpendicular to the x-direction. If the electrons are the main transporters of heat, we are able to calculate their contribution as follows.

$$\tfrac{1}{2}mu^2 = \tfrac{3}{2}kT \tag{11.15}$$

or

$$k\frac{\partial T}{\partial x} = \frac{1}{3}\frac{\partial}{\partial x}(mu^2). \tag{11.15a}$$

Each electron carries with it a surplus of energy

$$-\lambda\frac{\partial}{\partial x}\left(\frac{1}{2}mu^2\right)$$

in comparison with the electrons in the region where their directed motion is again spoiled. A similar gain in energy is obtained from electrons moving the opposite way. The net balance equation therefore becomes

$$Q = -\frac{1}{3}nu\lambda\frac{\partial}{\partial x}\left(\frac{1}{2}mu^2\right), \tag{11.15b}$$

where Q is the heat transport per unit area in the x-direction. Inserting (11.15a), the result we obtain

$$Q = -\frac{1}{2}nk\lambda u\frac{\partial T}{\partial x} \tag{11.16}$$

which gives the heat conductivity

$$K = \tfrac{1}{2}n\lambda uk. \tag{11.16a}$$

The elements of the equation are almost obvious, in particular the proportionality of K with n, λ, and u. As in the formula for electric conductivity the dependence of u on temperature appears to be somewhat more dubious. Since electric and thermal conductivity have many features in common, it may be of particular interest to compare the two quantities by taking their ratio. From (11.14a) and (11.16a) we find, on using (11.15):

$$\frac{K}{\sigma} = \frac{mk}{e^2}u^2 = 3\frac{k^2}{e^2}T. \tag{11.17}$$

This is a most interesting result. It indicates that the ratio between heat and electric conductivity is the same for all metals at any temperature.

Obviously it cannot be expected to be an exact law, but approximately it fits surprisingly well. Its approximate independence of the metallic material of the conductor was discovered in 1853 by Wiedemann and Franz for which reason it is known as the Wiedemann-Franz law. The proportionality with absolute temperature was realized by L. Lorenz in 1882.

Proceeding more correctly in the calculation of the heat transport in classical calculation, we find that the proportionality factor in (11.17) reduces to $\frac{9}{4} = 2.25$, whereas in Fermi-Dirac statistics it is again raised to $\frac{1}{3}\pi^2 \simeq 3.3$. Actual values vary mostly between 3 and 4.

12. THE ELECTROMAGNETIC FIELD

The Origin and Basic Laws of Electromagnetism. The Biot-Savart and Ampère's Laws

The year 1820 is a remarkable milestone in the history of electricity and magnetism. In July of that year Hans Christian Ørsted (1777–1851) discovered the forces acting upon a magnet needle in the vicinity of a current-carrying metallic wire. In October of the same year André Marie Ampère (1775–1836) and also Jean Baptiste Biot (1774–1862), together with Felix Savart (1791–1841), presented their experimental and theoretical investigations of the same electromagnetic phenomenon which by Ampère was given the name *electromagnetism.*

The connection between current and field is astonishingly simple, as the elementary laws of nature usually are. It may, however, be expressed in formally different ways, one formulation following fairly easily from the other. We prefer to start with an elementary law called the *Biot-Savart law,*

$$d\mathbf{H} = \frac{J}{c}\frac{1}{r^2}\, d\mathbf{s} \times \hat{\mathbf{r}}, \qquad \hat{\mathbf{r}} = \frac{\mathbf{r}}{r}. \tag{12.1}$$

Here $d\mathbf{s}$ is the line element of a conducting wire in which flows a current J;

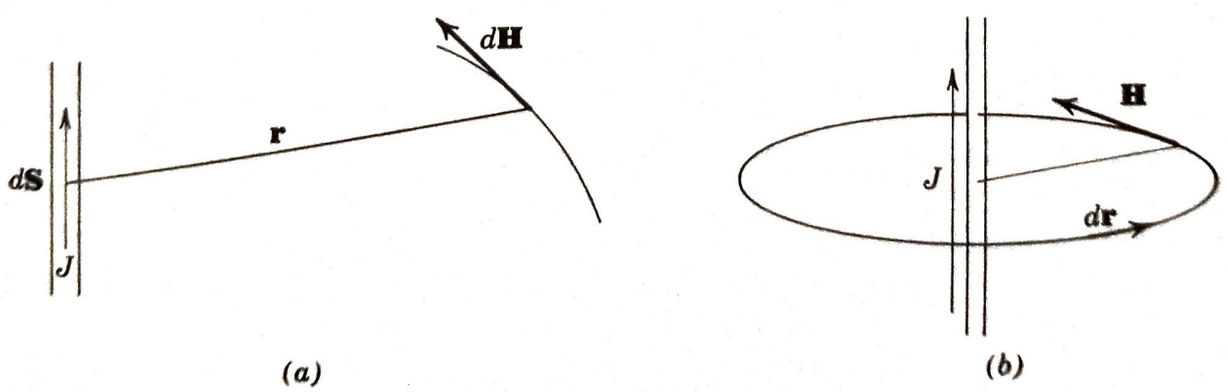

Fig. 2-2. (*a*) The field of a circular current according to the Biot-Savart law. (*b*) Magnetic field lines around a circular current of infinite length according to Ampère's law.

c is a factor of dimension velocity which will later on be identified with the velocity of light in vacuum. Hence $d\mathbf{H}$ presents the contribution to the magnetic field from the line element $d\mathbf{s}$ of a current circuit.

Steady currents are always closed currents. Therefore to some extent the elementary Biot-Savart law lacks the character of definiteness and should temporarily be replaced by the integral law

$$\mathbf{H} = \frac{J}{c} \oint \frac{d\mathbf{s} \times \mathbf{r}}{r^3} \tag{12.2}$$

with $d\mathbf{s}$ the line element of a closed current circuit. This is just the field (10.25) in which the vortex line is replaced by the circular conducting wire and the vortex strength M by J/c, the current strength in electromagnetic units. (See Fig. 2-2.)

From the considerations of Section 10, in particular, (10.25), (10.28), and (10.29), on replacing $\mathbf{B}$ by $\mathbf{H}$ and M by J/c it follows that

$$\oint \mathbf{H}\, d\mathbf{r} = 4\pi \frac{J}{c} \tag{12.3}$$

for any closed curve with line element $d\mathbf{r}$ encircling the conducting wire in a positive direction. The result is known as *Ampère's law*. For practical purposes, in particular for very simple spatial arrangements of currents, the Ampère form of the basic law of electromagnetism may allow for the easiest and most direct evaluation of the field. A typical example is the infinite linear wire (with very distant ends connected by some conducting device to close the current). Because of symmetry the magnetic field lines are circles centered on the wire and in planes perpendicular to the wire. Here the Ampère law directly gives the field strength

$$H = \frac{2J}{ac} \tag{12.3a}$$

at a distance a from the wire.

Since currents are never strictly linear, that is, of infinitely small cross sections, we have to replace the single linear current by an infinite number of currents of infinitesimal strength. We therefore have to replace the form (12.3) of Ampère's law by

$$\oint \mathbf{H}\, d\mathbf{r} = \frac{4\pi}{c} \int \mathbf{j}\, d\mathbf{S} \tag{12.4}$$

on expressing the current J inside the closed path of integration by a surface integral over the current density. The surface integral may then comprise the total cross section of the wire or, maybe, only a part of it. From this

equation one easily arrives at the differential equation for the electromagnetic field. For that purpose Ampère's law, that is, the integral form, is better suited than the Biot-Savart elementary law. Using Stokes' theorem,

$$\oint \mathbf{H}\, d\mathbf{r} = \int \operatorname{curl} \mathbf{H}\, d\mathbf{S} \tag{12.4a}$$

and contracting the line integral to encompass any small surface we find that the result is

$$\operatorname{curl} \mathbf{H} = \frac{4\pi}{c}\mathbf{j}. \tag{12.5}$$

This is the basic differential equation for the electromagnetic field of a given spatial distribution of stationary current density.

Calculations of Electromagnetic Fields

To illustrate the use of the various forms of basic electromagnetic laws consider first an infinitely long rectilinear conductor with circular cross section of radius a and a total current J. From Ampère's law we find directly the field strength

$$H_\varphi = \frac{J}{c}\begin{cases} \dfrac{2}{\rho}, & \rho > a \\[2ex] \dfrac{2\rho}{a^2}, & \rho < a \end{cases} \tag{12.6}$$

on denoting by H_φ the only nonvanishing component of $\mathbf{H}$ which is the tangential component to a circle of radius ρ around or inside the conductor.

Next consider the Biot-Savart law. Take first the formula (12.2) for a linear wire. With the origin somewhere on the wire and $d\mathbf{s}$ pointing in the z-direction it is seen that the only component to determine is

$$\begin{aligned} H_\varphi &= \frac{2J}{c}\int_0^\infty \frac{\rho\, dz}{(\rho^2 + z^2)^{3/2}} \\ &= \frac{2J}{c\rho}\left[\frac{z}{(\rho^2 + z^2)^{1/2}}\right]_0^\infty = \frac{2J}{c\rho}. \end{aligned} \tag{12.7}$$

In the case of a wire of finite radius a, considering for simplicity the field point $(\rho, 0, z_0)$, the calculations become more troublesome because the line integral (12.7) must be replaced by the volume integral

$$H_\varphi = \frac{J}{c}\frac{1}{\pi a^2}\int_{-\infty}^{\infty} dz \int_0^a \rho'\, d\rho' \int_0^{2\pi} d\varphi\, \frac{(\rho - \rho' \cos\varphi)}{[(z - z_0)^2 + (\rho - \rho'\cos\varphi)^2 + \rho'^2 \sin^2\varphi]^{3/2}} \tag{12.8}$$

with (ρ', φ, z) source point coordinates. The integral appears unduly complex. Fortunately the integration in z is simple as in (12.7) and gives

$$H_\varphi = \frac{2J}{c}\frac{1}{\pi a^2}\int_0^a \rho'\,d\rho'\int_0^{2\pi} d\varphi\,\frac{\rho - \rho'\cos\varphi}{(\rho - \rho'\cos\varphi)^2 + \rho'^2\sin^2\varphi} \tag{12.8a}$$

independent of z. Again the integral looks unwieldy, but rewriting the integrand in the form

$$\frac{1}{2}\left(\frac{1}{\rho - \rho' e^{-i\varphi}} + \frac{1}{\rho - \rho' e^{i\varphi}}\right),$$

we see that integration in φ gives zero if $\rho' > \rho$ and $2\pi/\rho$ when $\rho' < \rho$. Hence

$$H_\varphi = \frac{2J}{c\rho}\frac{2}{a^2}\int_0^{a,\rho} \rho'\,d\rho' = \begin{cases} \dfrac{2J}{c\rho}, & \rho > a, \\ \dfrac{2J\rho}{ca^2}, & \rho < a, \end{cases} \tag{12.9}$$

as in (12.6).

Finally consider the solving process for a linear wire by means of the vector potential

$$\mathbf{A} = \frac{J}{c}\oint \frac{d\mathbf{s}}{r}, \qquad \mathbf{H} = \operatorname{curl}\mathbf{A} \tag{12.10}$$

with A_z the only nonvanishing component. Outside the wire we have

$$\nabla^2 A_z = 0 \tag{12.10a}$$

with $A_z = A_z(\rho)$ independent of z and φ; hence

$$\frac{1}{\rho}\frac{d}{d\rho}\rho\frac{d}{d\rho}A_z = 0, \qquad A_z = b\log\rho + c. \tag{12.10b}$$

The constant c is insignificant, and b may be determined from $H_\varphi = -\partial A_z/\partial\rho = -b/\rho$ by means of Ampère's law. It may be also be determined by calculating the diverging integral of the vector potential on removing an infinite constant term,

$$A_z = \frac{2J}{c}\int_0^\infty \frac{dz}{(z^2 + \rho^2)^{1/2}} = -\frac{2J}{c}\log\rho, \tag{12.10c}$$

and hence obtain the correct value $b = -2J/c$. The φ-component of H becomes

$$H_\varphi = -\frac{\partial A_z}{\partial\rho} = \frac{2J}{c\rho} \tag{12.10d}$$

as before.

Now changing to the wire of finite radius a we have for A_z the same equation (12.10a) and the same solution (12.10b) as earlier when $\rho > a$. Inside the wire, $\rho < a$, we have the inhomogeneous equation

$$\nabla^2 A_z = -4\pi \frac{j}{c} = -\frac{2J}{c}\frac{2}{a^2}. \tag{12.11}$$

Here the logarithmic term must be discarded; so, if we want to fit the solution with (12.10c) at $\rho = a$, we have to take the definite solution

$$A_z = -\frac{2J}{c}\left(\frac{\rho^2}{2a^2} - \frac{1}{2} + \log a\right). \tag{12.11a}$$

This gives for $\rho < a$

$$H_\varphi = -\frac{\partial A_z}{\partial \rho} = \frac{2J}{c}\frac{\rho}{a^2} \tag{12.11b}$$

as before.

The above examples serve to illustrate a number of possible ways of handling the problem of evaluating electromagnetic fields rather than teaching how to do it in the most convenient manner.

Another problem which is easily solved by means of the integral Ampère law is that of a long-stretched solenoid. Take the axis to be in the z-direction and let the length of the solenoid be L. The number of windings from the same wire carrying a current J is N, so that $n = N/L$ is the number of turns per unit length. If the solenoid is of considerable length, the outside magnetic field is very faint. Neglecting this part and considering the inside field, we see that even Ampère's law gives approximately

$$LH_z = \frac{4\pi}{c} NJ, \tag{12.12}$$

independent of how far from the axis H_z is measured. This proves that the field is fairly homogeneous with faint ρ-components, if any. Because of axial symmetry there is no φ-component.

Usually the solenoid equation is written

$$H_z = \frac{4\pi}{c} nJ \tag{12.13}$$

with n the number of turns per unit length. It applies only to the ideal case of an infinitely long solenoid. In the ideal form, an only too well-known laboratory equation, it is not very exciting. Somewhat more interest may be found in the deviations of a real solenoid field from that of the ideal formula.

Consider an ordinary solenoid produced by cutting off at both ends and removing the rest part of an infinitely long solenoid. Obviously it corresponds to removing a magnetic pole plate of free magnetic surface density

$\mp nJ$ at either end. This is equivalent to placing magnetic plates of opposite sign $\pm nJ$ at either end. The parallel components of the solenoid magnetic field correspond to the normal components of the magnetic fields of the plates and are easily calculated in the same manner as the electrostatic field in (4.15). The result is

$$H_z = (4\pi - \Omega_+ - \Omega_-)\frac{nJ}{c} \tag{12.14}$$

with Ω_+ and Ω_- the solid angles of the end apertures as seen from an inside field point. In particular at the one end of the solenoid the z-component of the field drops approximately to half its inside value.

The same reasoning may be used to give an idea of the faint field outside a solenoid of given dimensions.

Ampère's Theory of Magnetism

The first one to prove the equivalence of a magnetic double layer and a closed circular current with respect to their magnetic fields was Ampère who also proposed an entirely new theory of magnetism. According to his view all elementary molecular magnets originate from circular currents within the atoms and molecules. Magnetization of a body hence consists of a forced anisotropic orientation of molecular circular currents.

As already mentioned experience forces us to discard the idea of isolated magnetic charge. For a long time the concept of elementary magnetic dipoles in the naïve picture of minute magnetic rods was also denied. The existence of the spinning magnetic electron has led to some doubt about the final true origin of magnetism owing to the anomalous gyromagnetic ratio of the Dirac electron. Since at all events the electron has a spin that allows for imagining it in the form of rotating electric charges, we shall be satisfied to accept the Ampère view, even though the mysteries of magnetism are evidently intimately connected with the existence of spinning magnetic electrons.

Consider the equation

$$M_0 = \frac{J_0 S_0}{c}\ , \tag{12.15}$$

the left-hand side representing a fictitious magnetic plate of dipole strength M_0, the right-hand side explaining it the other way as an electric current circuit J_0 comprising an area S_0. If for some reason the circuits are not oriented quite isotropically at random, their magnetic moments may be summed up vectorially to a resulting dipole density $\mathbf{M}$.

Now imagining a number of molecular circuits having quadratic shape and the same orientation, so that they may be put together side by side, the effect will be a current J_0 along their outer circumference. In this way we

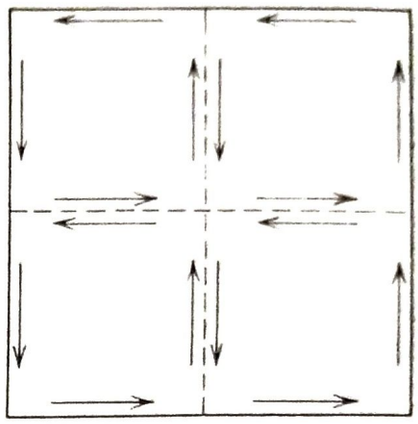

Fig. 2-3. Production of macroscopic free currents by the addition of molecular circular currents.

obtain the concept of macroscopic currents or current densities $\mathbf{j}''$ produced by the minute molecular current circuits. (See Fig. 2-3.) These macroscopic electric currents are fictitious in the same sense as fictitious charges in electrostatics. When added to convective or conductive currents $\mathbf{j}$, the result is a total current density

$$\mathbf{j}' = \mathbf{j} + \mathbf{j}'' \tag{12.16}$$

bearing the name of free current.

We now investigate the connection between the curl of the magnetization vector and the fictitious macroscopic current $\mathbf{j}''$. To that end we consider the line integral $\oint \mathbf{M}\, d\mathbf{s}$ along any closed curve in space. For simplicity we consider only the surplus of circuits giving the net component M_s in the direction $d\mathbf{s}$. For simplicity they may even be thought of as all having the orientation $d\mathbf{s}$. Their number being n per unit volume, we have $M_s = nM_0$. (See Fig. 2-4.)

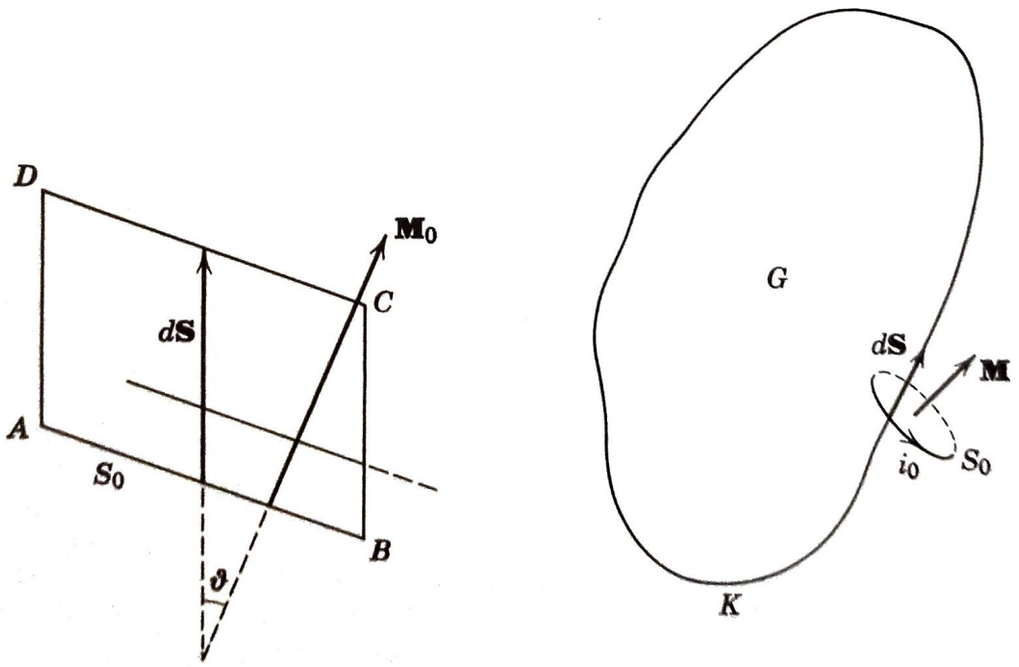

Fig. 2-4. Closed curve integrals of magnetization resulting from molecular currents encircling the curve.

The molecular currents encircling the integration curve are only those having their centers within an area S_0 around the curve. The net fictitious current sent through a surface bounded by the curve therefore is

$$\int \mathbf{j}'' d\mathbf{S} = \oint ds\, S_0 n J_0 = \oint ds\, c M_s \,. \tag{12.17}$$

Applying the Stokes theorem and contracting the curve, we arrive at the differential equation

$$\text{curl } \mathbf{M} = \frac{1}{c}\,\mathbf{j}''. \tag{12.17a}$$

From the connecting equation

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} \tag{12.17b}$$

we now obtain in addition to div $\mathbf{B} = 0$ the equation

$$\text{curl } \mathbf{B} = \text{curl } \mathbf{H} + 4\pi \text{ curl } \mathbf{M} = \frac{4\pi}{c}\,\mathbf{j}'. \tag{12.18}$$

This means that **B** is the true magnetic field in the interior of a magnetic body, whereas **H** is an auxiliary vector that corresponds to replacing the true molecular current circuit by equivalent fictitious magnetic double layers.

The Kelvin definition of **H** and **B** inside a magnetic body remains valid, however, even in the Ampère picture of magnetism.

13. ELECTRODYNAMICS

Reactive Forces as Derived from the Biot-Savart Law

According to the principle of *actio* and *reactio* the mechanical forces on a magnetic body from an electric current will be met with reactive forces on the conductor in which the current is flowing. We now apply the principle to the elementary Biot-Savart law

$$d\mathbf{H} = \frac{J}{c}\,\frac{d\mathbf{s} \times \mathbf{r}}{r^3}\,. \tag{13.1}$$

If we apply the law to a magnetic dipole, the result is a torque on the dipole, and this would lead to a fairly complex set of arguments. In magnetostatics we have to some extent, however, justified the procedure of reasoning as though isolated magnetic poles or magnetic charges were at our disposal. The expression (13.1) then is the force acting on a unit magnetic pole by the current-carrying line element $d\mathbf{s}$ of the conductor. According to our principle an equally strong force originating from the unit magnet pole must act in the opposite direction on the conductor element $d\mathbf{s}$.

Now the only way the magnetic pole can act upon the conductor is through its magnetic field at $d\mathbf{s}$ and this is $-\mathbf{r}/r^3$ with $\mathbf{r}$ pointing from $d\mathbf{s}$ to the magnetic pole. This result applies, however, only to empty space. If the space is filled with magnetic material of permeability μ, the magnetic field is weakened in the proportion $1:\mu$. The said field $-r/r^3$ therefore is the induction field $\mathbf{B}$ of the unit magnet pole and not the magnetic field $\mathbf{H}$. Remembering the opposite sign of the reaction force, we therefore advance the hypothesis that the reactive force on the conductor element $d\mathbf{s}$ is

$$d\mathbf{F} = \frac{J}{c} d\mathbf{s} \times \mathbf{B} \tag{13.2}$$

with $\mathbf{B}$ the above field from the magnetic pole.

Since the conductor element obeys the surrounding field unconscious of its origin, we therefore venture to accept (13.2) as the basic law for mechanical forces on current elements for induction fields $\mathbf{B}$ of whatever origin.

Potential Energy of a Current Circuit in a Magnetic Field

From a simple calculation of the potential energy of a circuit in a magnetic field we may possibly find even more convincing arguments. From the equivalence of a magnetic double layer and a current circuit we have found the magnetic potential of the circuit

$$U = \frac{I}{c} \Omega, \tag{13.3}$$

where Ω is the solid angle subtended by the positive side of the circuit as seen from the field point. The expression (13.3) then is also the potential of a unit magnet pole in that field. Note that according to the Biot-Savart law the result is independent of the permeability μ of the surrounding medium.

Now (13.3) is also the potential energy of the circuit in the field of the unit magnetic pole. But Ω is the number of magnetic field lines sent through the circuit in a direction from the positive to the negative side provided that we have $\mu = 1$ the vacuum value. With arbitrary μ, Ω is the number of induction lines. Again the circuit is unaware of the origin of the induction field, and hence its potential energy in an arbitary field must be

$$U = -\frac{J}{c} \int \mathbf{B}\, d\mathbf{S} \tag{13.4}$$

with $d\mathbf{S}$ vectorial elements of a surface surrounded by the circuit.

We now consider a circuit of a flexible conducting wire capable of having its elements $d\mathbf{s}$ displaced by vectorial elements $\delta\mathbf{s}$. This means that we are adding the surface elements

$$\delta(d\mathbf{S}) = d(\delta\mathbf{S}) = \delta\mathbf{s} \times d\mathbf{s} \tag{13.5}$$

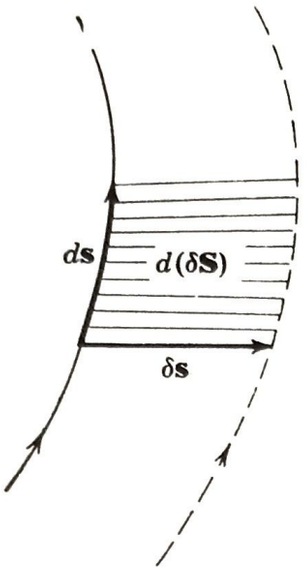

Fig. 2-5. Illustration by a current-carrying flexible wire of the Lorentz force of electro-magnetism and the potential energy of a current circuit in a magnetic field.

to our surface of integration and that the potential energy is changed by an amount

$$\delta U = -\frac{J}{c}\oint \delta\mathbf{s}(d\mathbf{s} \times \mathbf{B}). \tag{13.5a}$$

The work done on the wire by the interaction of the current and the magnetic field is $-\delta U$. Hence

$$\frac{1}{c} J\, d\mathbf{s}(\delta\mathbf{s} \times \mathbf{B})$$

may be taken to be the work done on the individual elements of the wire. The mechanical force acting upon the element $d\mathbf{s}$ hence is

$$d\mathbf{F} = \frac{J}{c} d\mathbf{s} \times \mathbf{B} \tag{13.6}$$

as in (13.2).

Forces on Moving Charges

Consider a concentrated charge e moving within the wire with velocity $\mathbf{v} = d\mathbf{s}/dt$ where the length of $d\mathbf{s}$ or the time interval is adapted to the velocity $\mathbf{v}$. Then for that single charge J corresponds to de/dt so that

$$J\, d\mathbf{s} = e\mathbf{v}. \tag{13.7}$$

Hence the mechanical force on the charge in the induction field is

$$\mathbf{F} = \frac{e}{c}\mathbf{v} \times \mathbf{B}. \tag{13.7a}$$

If e is the charge of a single particle like the electron, this is the renowned Lorentz force in electron theory.

Considering the motion of a continuous charge distribution as expressed either by its velocity $\mathbf{v}$ or the resulting current density $\mathbf{j} = \rho\mathbf{v}$, we find that the force referred to unit volume becomes

$$\mathbf{F} = \frac{1}{c}\mathbf{j} \times \mathbf{B} = \frac{1}{c}\rho\mathbf{v} \times \mathbf{B}. \tag{13.8}$$

Mutual Potential Energy of Current-Carrying Circuits

Consider two circuits indicated as 1 and 2 or more generally i and k. We want to know their mutual potential energy for given currents J_i and J_k, the zero level being as usual when they are at infinite distance with no mechanical interaction.

The magnetic field of the current J_i is

$$\mathbf{H}_i = \text{curl } \mathbf{A}_i, \qquad \mathbf{A}_i = \frac{J_i}{c}\oint \frac{d\mathbf{s}_i}{\mathrm{r}_i}, \tag{13.9}$$

where r_i is the field point distance from $d\mathbf{s}_i$. The corresponding induction field in the region of the circuit k with permeability μ of the surrounding matter is $\mathbf{B}_i = \mu\mathbf{H}_i$ or

$$\mathbf{B}_i = \mu \text{ curl } \mathbf{A}_i = \text{curl } \mu\mathbf{A}_i. \tag{13.9a}$$

As we have seen the potential energy of a current-carrying circuit in an induction field $\mathbf{B}$ is minus the number of induction lines sent through the circuit in a positive direction times the current strength in electromagnetic units. Hence the potential energy becomes

$$U_{ik} = -L_{ik}J_iJ_k, \tag{13.10}$$

where L_{ik} is called the mutual induction coefficient or inductance of the two circuits.

It is easily found that

$$J_iL_{ik} = \frac{\mu}{c}\int \text{curl } \mathbf{A}_i \, d\mathbf{S}_k$$

$$= \frac{\mu}{c}\oint \mathbf{A}_i \, d\mathbf{s}_k \tag{13.10a}$$

from which, inserting (13.9) and dividing by J_i, we have

$$L_{ik} = \frac{\mu}{c^2}\oint\oint \frac{d\mathbf{s}_i \, d\mathbf{s}_k}{r_{ik}}. \tag{13.11}$$

14. NONSTATIONARY FIELDS AND ELECTROMAGNETIC INDUCTION

Faraday's Law of Induction

The mechanical forces on magnets or current-carrying circuits as originating from a given circuit are forces trying to set in motion the said magnets or circuits. On reasoning from principles like that of actio and reactio we might guess that motion of magnets or current circuits, that is, changes of the magnetic field around a given current circuit, might tend to establish a current in the circuit which means that an electromotive force is created in the circuit.

A well-defined statement of such a principle was given by Heinrich Friedrich Emil Lenz (1804–1865) in 1834, shortly after the discovery of electromagnetic induction which was made independently by Faraday in 1831 and Joseph Henry (1797–1878) in 1832. In addition the phenomenon of self-induction in current circuits was discovered by Henry for which reason coefficients of self-induction and of mutual induction as well are given in units called the henry.

The principle stated in Lenz's law was that induced electric currents are directed so as to set up resistance to changes causing the induction, whether of the nature of moving magnets and current circuits or of varying electric currents in the circuits. Of course, the ideas were mainly the same as those leading Faraday to perform his famous experimental proof of the induction. (See Fig. 2-6.)

If we denote by N the number of induction lines through a circuit

$$N = \int \mathbf{B}\, d\mathbf{S}, \tag{14.1}$$

the Faraday law of electromagnetic induction reads

$$E = -\frac{1}{c}\frac{dN}{dt}, \tag{14.2}$$

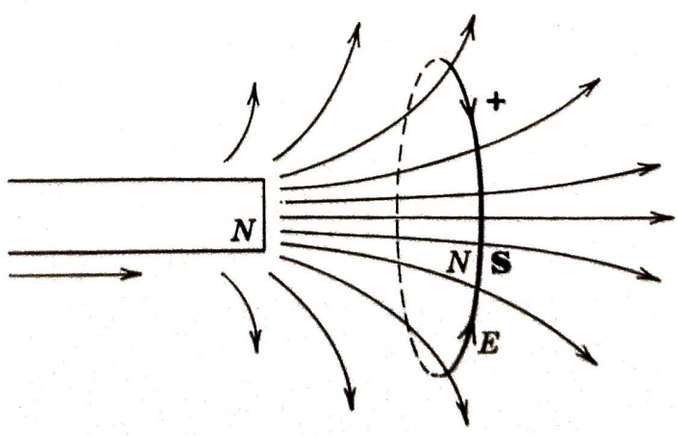

Fig. 2-6. Illustration of the Lenz law and the Faraday law of induction.

where E is the electromotive force of the circuit similar to that of a galvanic element introduced into the circuit. The law is numerically correct as will now be shown on basing the interpretation of inductive forces on the Lorentz force on moving charges or, say, charged atomic particles.

Induction Law as a Consequence of Lorentz Forces

In the deduction of mechanical forces on current-carrying conducting wires let

$$\delta \mathbf{s} = \mathbf{v}\, dt \tag{14.3}$$

be the displacement of a wire element $d\mathbf{s}$. A unit charge transported with the above velocity $\mathbf{v}$ by the conductor will experience a Lorentz force

$$\mathbf{E} = \frac{1}{c}\mathbf{v} \times \mathbf{B} = \frac{1}{c\, dt}\delta \mathbf{s} \times \mathbf{B} \tag{14.4}$$

in the induction field $\mathbf{B}$. The electromotive force along the element will be

$$\mathbf{E}\, d\mathbf{s} = -\frac{1}{c\, dt}\mathbf{B}(\delta \mathbf{s} \times d\mathbf{s}). \tag{14.5}$$

Now, as easily understood from previous considerations,

$$dN = \oint \mathbf{B}(\delta \mathbf{s} \times d\mathbf{s}) \tag{14.6}$$

is the increase of induction lines through the circuit. Hence

$$E = \oint \mathbf{E}\, d\mathbf{s} = -\frac{1}{c}\frac{dN}{dt} \tag{14.7}$$

which is the Faraday law.

Differential Equation Expressing the Faraday Law

The above deduction of Faraday's law, of course, is of restricted validity as based on the motion of circuit elements $d\mathbf{s}$ in a stationary induction field $\mathbf{B}$. It attains, however, a wide generalization by the requirement of invariance against Galilei transformations. This proves that electromotive forces in a circuit depend only on the relative motion of the circuit and the magnets or circuits producing the magnetic field. If requiring invariance also against rotational motion, the induction law can be referred to a circuit fixed in space; we must require the law to hold irrespective of the nature of the sources of the number N of induction lines, as well as the cause of their time variation.

Consider now a closed rigid curve in space under changes of the induction flux through the curve. The electromotive force around the curve must exist

whether movable charges like electrons are present or not, that is, whether or not a conducting wire with inside electrons follows the curve. We therefore have

$$\oint \mathbf{E}\, d\mathbf{s} = -\frac{1}{c}\frac{d}{dt}\int \mathbf{B}\, d\mathbf{S}. \tag{14.8}$$

On transforming the left-hand integral by Stokes' theorem and using inside time differentiation on the right-hand side, as allowed by a rigid boundary of the surface, we have

$$\int \operatorname{curl} \mathbf{E}\, d\mathbf{S} = -\frac{1}{c}\int \frac{\partial \mathbf{B}}{\partial t}\, d\mathbf{S}. \tag{14.9}$$

The equation is valid for any small surface in space. Hence we obtain the differential equation

$$\operatorname{curl} \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} \tag{14.10}$$

which is the fully prepared Maxwell equation expressing the induction law.

Mutual Inductances and Self-Inductance of Current Circuits

Consider a number of current-carrying circuits $i = 1, 2, \cdots, n$, with currents J_i; they will each produce their particular fields proportional in strength to the currents J_i. The number of induction lines through a particular circuit becomes

$$\frac{1}{c} N_i = \sum_k L_{ik} J_k. \tag{14.11}$$

The coefficients L_{ik} of the equation are called inductances or mutual inductances, except for L_{ii} which is called the self-inductance of the individual circuit i.

From the calculation of mutual potential energies of the previous section it is easily found that for any two circuits considered linear conductors the result is

$$L_{ik} = \frac{\mu}{c^2} \oint\oint \frac{d\mathbf{s}_i\, d\mathbf{s}_k}{r_{ik}} \tag{14.12}$$

as given in (13.11).

The formula usually is accurate enough even for conductors of some finite cross section, except maybe for particular refined measurements. For the evaluation of self-inductances, however, it fails entirely because of the non-convergence of the integral. This means that self-inductances are very sensitive to the cross section of the conducting wire. Fortunately, however, induction circuits are usually produced in the form of coils with a great

number of windings requiring considerable space in order to strengthen inductive electromotive forces. Whereas this may impede the theoretical evaluation of mutual inductances, the evaluation of self-inductances becomes at least feasible, if not easy. This is because the coil is fairly well represented by a continuous current distribution spread out over the total cross section of the coil.

Taking into consideration the cross section q_i of the coil or of a single circuit as well, whose cross section is at least finite, we may write the formula for self-inductance with considerable accuracy as

$$L_{ii} = \frac{\mu}{c^2} \oint\oint \frac{\cos \vartheta \, d\tau_i \, d\tau_i'}{q_i q_i' r} \tag{14.13}$$

on putting $d\mathbf{s}_i \, d\mathbf{s}_i' = \cos \vartheta \, ds_i \, ds_i'$, $d\tau_i = q_i \, ds_i$, $d\tau_i' = q_i' \, ds_i'$, and taking r to be the distance between the two volume elements. The cross section may even vary along the circuit, and the formula may be exact, provided that the current density is constant over individual cross sections.

Electromotive Forces in Current Circuits and Field Energy

Consider the current circuits in rigid positions so that no mechanical work is done. By slow variations of the currents the electromotive forces in the circuits are

$$E_i = -\frac{dN}{dt} = -\sum_k L_{ik} \frac{dJ_k}{dt}. \tag{14.14}$$

The work performed by the electromotive forces during an interval dt must be taken from the energy U_m of the field. Hence

$$-dA = -\sum_i E_i J_i \, dt = dU_m \tag{14.14a}$$

or

$$\sum_{ik} L_{ik} J_i \, dJ_k = dU_m. \tag{14.14b}$$

Hence the field energy

$$U_m = \frac{1}{2} \sum_{ik} L_{ik} J_i J_k. \tag{14.15}$$

Writing $J_i = q_i j_i$, $J_i \, d\mathbf{s}_i = \mathbf{j}_i \, d\tau_i$, we easily find from the inductance formula for L_{ik}, whether a mutual inductance or a self-inductance, that (14.15) can be changed into an exact double volume integral

$$U_m = \frac{\mu}{2c^2} \iint \frac{\mathbf{j}\mathbf{j}' \, d\tau \, d\tau'}{r}. \tag{14.15a}$$

Next, on generalizing the vector potential for a single circuit as given, for instance, in (13.9) into

$$\mathbf{A} = \frac{\mu}{c} \int \frac{\mathbf{j}'\, d\tau'}{r}, \tag{14.15b}$$

as valid for any number of circuits, and with the understanding that after multiplication with μ we now have curl $\mathbf{A} = \mathbf{B}$, the final result is

$$U_m = \frac{1}{2c} \int \mathbf{A}\mathbf{j}\, d\tau. \tag{14.16}$$

Once more we make a transformation writing

$$\mathbf{B} = \operatorname{curl} \mathbf{A}, \qquad \mathbf{j} = \frac{c}{4\pi} \operatorname{curl} \mathbf{H} \tag{14.17}$$

and apply the formula

$$\operatorname{div} (\mathbf{A} \times \mathbf{H}) = \mathbf{H} \operatorname{curl} \mathbf{A} - \mathbf{A} \operatorname{curl} \mathbf{H}. \tag{14.17a}$$

On inserting for $\mathbf{A}$ curl $\mathbf{H}$ and converting the divergence integral into a vanishing surface integral at infinite distance, the result is the volume integral over the entire space

$$U_m = \frac{1}{8\pi} \int \mathbf{H}\mathbf{B}\, d\tau. \tag{14.18}$$

This then is the basic formula for the magnetic field energy which presents the magnetic field energy as given by a space density

$$u_m = \frac{1}{8\pi} \mathbf{H}\mathbf{B} \tag{14.18a}$$

in accordance with previous results from consideration of work spent to produce a magnetic field.

Forces and Torques on Current Circuits. Mechanical Energy in Relation to Field Energy

As seen from (14.15) the contribution to the field energy from the interaction of two circuits i and k is $L_{ik}J_iJ_k$. One may be surprised then to learn from (13.10) that the mechanical potential energy of the same circuits has just the opposite value $-L_{ik}J_iJ_k$. This calls for some explanatory remarks.

When a movable circuit or coil is doing mechanical work on changing its position in space from negative to positive induction flux through the coil, the field energy has increased, which may appear a contradiction. The description of the process is incomplete, however, in assuming the currents

of the circuits to be constant. To maintain constant current, external electromotive forces must be applied to keep balance with the electromotive forces in the circuits as induced by the motion of the coil.

If ζ is a general position coordinate of the coil i, the generalized force (translatory force, torque, etc.) from the coil k is

$$F_{ik} = -\frac{\partial U_{ik}}{\partial \zeta} = J_i J_k \frac{\partial L_{ik}}{\partial \zeta} . \tag{14.19}$$

The work done by mechanical forces of electromagnetic origin is

$$F_{ik}\, d\zeta = J_i J_k\, dL_{ik}. \tag{14.19a}$$

The external electromotive forces to be applied in the two coils in consideration to keep the currents constant are

$$E_i = J_k \frac{dL_{ik}}{dt}, \qquad E_k = J_i \frac{dL_{ik}}{dt} . \tag{14.20}$$

The work done by those electric forces when the currents J_i and J_k are running is

$$(E_i J_i + E_k J_k)\, dt = 2 J_i J_k\, dL_{ik}. \tag{14.21}$$

This is twice the amount needed for mechanical work. There still remains a surplus work $J_i J_k\, dL_{ik}$ to account for the increased field energy because of the increase dL_{ik} of the inductance L_{ik}.

15. CHARGE AND ENERGY BALANCE IN SLOW-VARYING FIELDS

Magnetic Field Energy

So far there has been a considerable amount of common sense reasoning in our investigations of what field energy ought to be. In this way, believing in the differential equations already obtained for the electromagnetic field and the phenomenon of induction, namely,

$$\operatorname{curl} \mathbf{H} = \frac{4\pi}{c} \mathbf{j} \tag{15.1}$$

and

$$\operatorname{curl} \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \tag{15.2}$$

we are already in a position to state the results more definitely.

In allowing for variations of the magnetic field we are already in the domain of time-dependent processes. In principle, however, we first restrict our considerations to infinitely slow variations of the fields—in technical

terms, the quasistationary field—which means that second-order time derivatives are entirely neglected. This may be thought of as something similar to adiabatic processes in thermodynamics.

Using the formula (14.17*a*) with **A** replaced by **E** and considering (15.1) and (15.2), we find

$$\frac{c}{4\pi}\operatorname{div}(\mathbf{E}\times\mathbf{H}) = -\frac{1}{4\pi}\mathbf{H}\frac{\partial\mathbf{B}}{\partial t} - \mathbf{E}\mathbf{j}. \tag{15.3}$$

The time independence of μ suffices to ensure the validity of the equation $\mathbf{H}\,\partial\mathbf{B}/\partial t = \mathbf{B}\,\partial\mathbf{H}/\partial t$. On integrating over the entire space and converting the left-hand integral into a vanishing surface integral at infinity, the result is

$$\frac{1}{8\pi}\frac{d}{dt}\mathbf{HB}\int d\tau + \int \mathbf{E}\mathbf{j}\,d\tau = 0. \tag{15.4}$$

This is an energy balance equation. The second integral is known to represent the time rate of work done on electric charges by the field as usually converted into heat energy. The energy must be taken from somewhere and there is no other source of energy than the magnetic field. This fits accurately with our previous deduction of magnetic field energy

$$u_m = \frac{1}{8\pi}\mathbf{HB}, \qquad U_m = \int u_m\,d\tau. \tag{15.5}$$

Equation 4.15 then becomes

$$\int \mathbf{E}\mathbf{j}\,d\tau = -\frac{dU_m}{dt}. \tag{15.5a}$$

Maxwell's Displacement Current

Inspecting the basic equations (15.1) and (15.2), we find that in virtue of the general law $\operatorname{div}\mathbf{B} = 0$ (15.2) may be generally true, whereas (15.1) cannot. This follows from the equation of continuity

$$\operatorname{div}\mathbf{j} = -\frac{\partial\rho}{\partial t} \tag{15.6}$$

in the case of any kind of accumulation of electric charges. An excellent example of nonclosed electric currents is provided by the charging or discharging of a plate accumulator. The illustration by this or similar examples may be instructive but may very well be dispensed with, since in the differential equation of electrostatics

$$\operatorname{div}\mathbf{D} = 4\pi\rho, \tag{15.7}$$

we have the easiest means of obtaining a thrustworthy generalization of (15.1). From the above equation we have on writing

$$\mathbf{j}_D = \frac{1}{4\pi}\frac{\partial \mathbf{D}}{\partial t} \tag{15.8}$$

the divergence equation

$$\operatorname{div}(\mathbf{j} + \mathbf{j}_D) = 0. \tag{15.9}$$

Hence a possible generalization of (15.1) is

$$\operatorname{curl} \mathbf{H} = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t}. \tag{15.10}$$

This is the famous and exceptionally important generalization of Ampère's law by Maxwell, as based on the concept of displacement currents $\mathbf{j}_D$ as expressed in (15.8). In fact (15.8) is partly true also in our naïve concept of electric currents. Inserting in (15.8) the expression $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$, we have

$$\mathbf{j}_D = \frac{1}{4\pi}\frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t}. \tag{15.11}$$

Now $\mathbf{P}$ means literally transport or displacement of charges. Hence the last term is a true electric current density. The first term, however, still belongs to the secrets of the vacuum as manifested by the full set of Maxwell's electromagnetic equations.

The introduction of Maxwell's displacement current allows for an interesting generalization of the energy principle inasmuch as the Joule heat of the electric current in (15.5*a*) may be thought of as drawn from both the electric and magnetic field energy. This is very easily demonstrated in accepting the Maxwell equation (15.10).

We may as well turn it the other way on replacing (15.5*a*) by

$$\int \mathbf{E}\mathbf{j}\, d\tau = -\frac{dU_m}{dt} - \frac{dU_e}{dt} \tag{15.12}$$

with the already accepted electric field energy

$$U_e = \frac{1}{8\pi}\int \mathbf{E}\mathbf{D}\, d\tau. \tag{15.12a}$$

We now rewrite (15.12) in the form

$$\int \left[\frac{4\pi}{c}\mathbf{j}\mathbf{E} + \frac{1}{c}\left(\mathbf{H}\frac{\partial \mathbf{B}}{\partial t} + \mathbf{E}\frac{\partial \mathbf{D}}{\partial t}\right)\right] d\tau = 0 \tag{15.13}$$

with the integration extended over the entire space.

On inserting for $\partial \mathbf{B}/\partial t$ from (15.2) and using the equation

$$\operatorname{div}(\mathbf{E} \times \mathbf{H}) = \mathbf{H} \operatorname{curl} \mathbf{E} - \mathbf{E} \operatorname{curl} \mathbf{H}, \tag{15.14}$$

we find

$$\int \mathbf{E}\left(\frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} - \operatorname{curl} \mathbf{H}\right) d\tau = 0 \tag{15.14a}$$

on removing the zero integral over div $(\mathbf{E} \times \mathbf{H})$. Even though it is not fully convincing without some additional arguments, the equation suggests very strongly that the Maxwell equation (15.10) is a consequence of energy principles.

Energy Transport by Radiation

Consider the energy balance equation for a region bounded by a closed surface with vectorial surface elements denoted by $d\boldsymbol{\sigma}$

$$\int \frac{c}{4\pi}(\mathbf{E} \times \mathbf{H})\, d\boldsymbol{\sigma} + \int \left(\mathbf{E}\mathbf{j} + \frac{\partial u_m}{\partial t} + \frac{\partial u_e}{\partial t}\right) d\tau = 0. \tag{15.15}$$

This means that if the three last energy terms of already well-known interpretation are not in perfect balance, energy must pass in or out through the boundary surface by some as yet not described process for which the first term is responsible. This term depends only upon field quantities and can only represent field energy. We are therefore led to the concept of field energy in motion, that is, electromagnetic radiation.

The vector

$$\mathbf{S} = \frac{c}{4\pi}(\mathbf{E} \times \mathbf{H}) \tag{15.16}$$

is called the Poynting vector after the discoverer of its importance. (See Figs. 2-7*a* and 2-7*b*.) Writing $\partial w/\partial t = \mathbf{E}\mathbf{j}$ for the local time rate of production of Coulomb heat w, and contracting the boundary surface around a field point in space, (15.15) becomes

$$\operatorname{div} \mathbf{S} + \frac{\partial}{\partial t}(w + u) = 0. \tag{15.17}$$

This is the energy conservation law or the continuity equation of energy. The Poynting vector therefore is the transport vector for radiative energy. Its outstanding importance in radiation theory is well known and will be frequently demonstrated in what follows. It may, however, be illustrated here in an apparently curious way in examples from stationary problems.

Consider for instance a straight wire of radius a carrying a current J. If $E = -dV/dz$ is the electric field inside the wire, the rate of heat production per unit length of the wire is $dW/dt = EJ$; however, $dW/dt = EJr^2/a^2$ if only a part of the cross section inside of $r < a$ is considered.

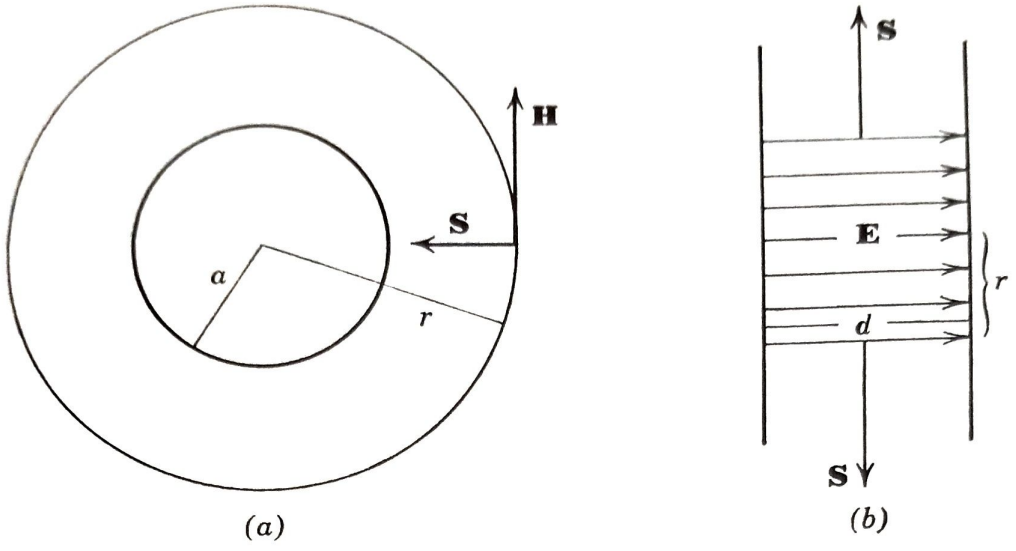

Fig. 2-7. (*a*) Transport of energy from the magnetic field into a current-carrying wire according to the Poynting theorem. (*b*) Corresponding dissipation of field energy from a plate condenser of decreasing charge.

From our previous investigations we have according to Ampère's law:

$$H = \frac{2J}{c}\begin{cases}\dfrac{1}{r}, & (r > a),\\[2ex] \dfrac{r}{a^2}, & (r < a).\end{cases} \tag{15.18}$$

Inserting for J, we have in either case

$$\frac{dW}{dt} = \frac{c}{4\pi} EH\,2\pi r. \tag{15.18a}$$

Since **E** and **H** are mutually orthogonal with **E** × **H** normal to the wire surface in inward direction, the result may be written

$$\frac{dW}{dt} = -\frac{c}{4\pi}\left(\int \mathbf{E} \times \mathbf{H}\right) d\sigma. \tag{15.19}$$

This equation maintains that the heat energy produced in the wire is traveling into the wire from the outside sources of field energy. Even though apparently confusing and from a practical point of view somewhat dubious there is no doubt that the result is intimately connected with fundamental laws of nature.

16. MECHANICAL PROPERTIES OF RADIATION

The Generalized Maxwell Stress Tensor

In Chapter 1 we studied the stress tensor of electrostatics leaving it to the reader to infer that the corresponding tensor of magnetostatics would have the same form.

We are now in the position not only of being able to remove this lack of completeness but also to draw useful conclusions about significant properties of electromagnetic radiation.

To that end we write from our adopted formula from electrostatics, magnetostatics, and electromagnetism the force acting per unit volume on electric charges and dielectric and magnetic bodies, namely,

$$\mathbf{F} = \rho\mathbf{E} + \frac{1}{c}\mathbf{j} \times \mathbf{B} - \frac{1}{8\pi}(\mathbf{E}^2\nabla\varepsilon + \mathbf{H}^2\nabla\mu), \tag{16.1}$$

the last terms being needed only for inhomogeneous matter. Our aim is to have expressions depending only on the field variables (as we shall see the dependence on ε and μ will also disappear).

We therefore eliminate ρ and $\mathbf{j}$ by the electrostatic and electromagnetic equations

$$\rho = \frac{1}{4\pi}\operatorname{div}\mathbf{D}, \qquad \mathbf{j} = \frac{c}{4\pi}\operatorname{curl}\mathbf{H} - \frac{1}{4\pi}\frac{\partial\mathbf{D}}{\partial t} \tag{16.1a}$$

and obtain

$$8\pi\mathbf{F} = 2\mathbf{E}\operatorname{div}\mathbf{D} - \mathbf{E}^2\nabla\varepsilon + 2\operatorname{curl}\mathbf{H} \times \mathbf{B} - \mathbf{H}^2\nabla\mu - \frac{2}{c}\frac{\partial\mathbf{D}}{\partial t} \times \mathbf{B}. \tag{16.1b}$$

On adding for symmetry purposes the zero expressions

$$2\mathbf{H}\operatorname{div}\mathbf{B} = 0, \qquad 2\left(\operatorname{curl}\mathbf{E} + \frac{1}{c}\frac{\partial\mathbf{B}}{\partial t}\right) \times \mathbf{D} = 0, \tag{16.1c}$$

the result is

$$\begin{aligned} 8\pi\mathbf{F} = {} & 2\mathbf{E}\operatorname{div}\mathbf{D} - \mathbf{E}^2\nabla\varepsilon + 2\operatorname{curl}\mathbf{E} \times \mathbf{D} \\ & + 2\mathbf{H}\operatorname{div}\mathbf{B} - \mathbf{H}^2\nabla\mu + 2\operatorname{curl}\mathbf{H} \times \mathbf{B} \\ & - \frac{2}{c}\frac{\partial}{\partial t}(\mathbf{D} \times \mathbf{B}). \end{aligned} \tag{16.2}$$

Analyzing more detailed components, say, the x-component, we find that

$$8\pi F_x = \operatorname{div}[2E_x\mathbf{D} + 2H_x\mathbf{B} - \mathbf{i}(\mathbf{ED} + \mathbf{HB})] - \frac{2}{c}\frac{\partial}{\partial t}(\mathbf{D} \times \mathbf{B})_x. \tag{16.3}$$

Introducing the electromagnetic momentum density vector

$$\mathbf{g} = \frac{1}{4\pi c}(\mathbf{D} \times \mathbf{B}), \tag{16.4}$$

and integrating for each component of $\mathbf{F}$ and $\partial\mathbf{g}/\partial t$ inside a closed surface in space, we find the result

$$\int\left(\mathbf{F} + \frac{\partial\mathbf{g}}{\partial t}\right)d\tau = \int T\,d\boldsymbol{\sigma}. \tag{16.5}$$

Here $d\boldsymbol{\sigma} = \mathbf{n}\, d\sigma$ is a vectorial surface element with an outer positive normal $\mathbf{n}$ and T is the Maxwell stress tensor

$$T = \frac{1}{8\pi}\,[2\mathbf{E}\cdot\mathbf{D} + 2\mathbf{H}\cdot\mathbf{B} - I(\mathbf{ED} + \mathbf{HB})] \tag{16.6}$$

with $\mathbf{E}\cdot\mathbf{D}$, and so forth, dyadic products and I the unit tensor.

Connections Between the Momentum Density of Radiation and the Poynting Vector

We have now in (16.6) regained the full Maxwell stress tensor for the electromagnetic field. The right-hand expression (16.5) represents the total outside force acting on a boundary region in space. According to this equation the force is converted into a force $\mathbf{F}$ acting on volume elements of the body, producing acceleration, and in addition a volume force $\partial\mathbf{g}/\partial t$, which according to (16.4) is connected only with radiation.

Since force is the time derivative of momentum, the vector $\mathbf{g}$ means momentum density, that is, momentum density of radiation. The connection with the Poynting vector or radiation vector

$$\mathbf{S} = \frac{c}{4\pi}(\mathbf{E}\times\mathbf{H}) \tag{16.7}$$

is

$$\mathbf{g} = \frac{\varepsilon\mu}{c^2}\,\mathbf{S}. \tag{16.8}$$

Let it be known that in a pure radiation field $\mathbf{E}$ and $\mathbf{H}$ are mutually orthogonal vectors. Then $\mathbf{S}$ and $\mathbf{g}$ are orthogonal to both of them. In addition the succession $\mathbf{E}$, $\mathbf{H}$, $\mathbf{S}$ forms the axis of a right-hand coordinate system with $\mathbf{S}$ and $\mathbf{g}$ pointing in the direction of radiation. Furthermore, let it be known that the velocity of propagation of radiation is

$$v = \frac{c}{n}, \qquad n = \sqrt{\varepsilon\mu}, \tag{16.9}$$

where n is the so-called refraction index. The connection between energy density, energy transport, and momentum density in directed radiation is

$$g = \frac{S}{v^2} = \frac{u}{v}. \tag{16.10}$$

Momentum and Energy of Photons

Consider particles obeying the laws of Newtonian mechanics, with mass m and velocity v. Their energy and momentum are

$$U = \tfrac{1}{2}mv^2, \qquad G = mv \tag{16.11}$$

yielding the relation

$$G = \frac{2U}{v} . \tag{16.11a}$$

This excludes any corpuscular interpretation of electromagnetic radiation on the basis of Newtonian mechanics. The situation in relativistic mechanics is, however, quite different. The relativistic energy and momentum of a free particle are

$$U = mc^2, \qquad G = mv, \tag{16.12}$$

with

$$m = \frac{m_0}{(1 - v^2/c^2)^{1/2}} \tag{16.12a}$$

the velocity-dependent mass of the particle. Hence the relation

$$G = \frac{v}{c^2} U, \tag{16.13}$$

which for particles traveling with the speed of light, $v = c$, unites (16.10) and (16.13) into the same result. This at least does not exclude the possibility of interpreting electromagnetic radiation as a stream of particles called photons or light quanta in quantum theory.

According to this theory the energy of a single photon of frequency ν is

$$E = h\nu \tag{16.14}$$

with h the quantum of action. Hence the momentum

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{16.15}$$

or

$$\lambda = \frac{h}{p}, \tag{16.15a}$$

and this is also the well-known de Broglie wavelength of material particles if the dualism wave particle is extended into the realm of material atomic particles.

Energy Density and Radiation Pressure of Electromagnetic Radiation

Consider a unit cube volume with reflecting walls filled with a radiation of density u. For our present purpose we roughly divide the isotropic radiation into three parts, each of them traveling with the speed of light in the direction of a particular coordinate axis. This procedure leads to correct results for momentum exchange. The right-hand wall is hit $n = c/2$ times by the same

radiation quantum per unit time, exchanging thereby an amount of momentum twice its momentum u/c by ideal reflection. In the case of partial or total absorption one obtains exactly the same result provided the radiation is in thermal equilibrium with the walls. The force per unit area, that is, the pressure therefore is

$$p = \frac{1}{3}\frac{c}{2}\frac{2}{c}u = \frac{1}{3}u, \tag{16.16}$$

and this is in fact the true value of radiation pressure. The considerations may be refined so as to prove the above result valid in the case of absorption and even at reduced speed of the radiation owing to the material constants ε and μ differing from unity.

Looking into the matter from the side of the Maxwell stress tensor, we may again consider the right-hand surface orthogonal to the x-axis with the inside normal considered the positive normal $\mathbf{n} = (-1, 0, 0)$. The stress on this surface is then

$$T\mathbf{n} = -\frac{1}{8\pi}[2\mathbf{E}D_x + 2\mathbf{H}B_x - \mathbf{i}(\mathbf{ED} + \mathbf{HB})]. \tag{16.17}$$

With isotropic radiation, $\overline{E_y D_x} = 0$, and so forth, the y and z components have zero mean values. The normal component of stress is obtained by multiplying over again with $\mathbf{n}$,

$$\mathbf{n}T\mathbf{n} = \frac{1}{8\pi}[2E_x D_x + 2H_x B_x - (\mathbf{ED} + \mathbf{HB})]. \tag{16.17a}$$

On averaging over the isotropic radiation on putting $\overline{E_x D_x} = \frac{1}{3}\overline{\mathbf{ED}}$, and so forth, the result is

$$\overline{\mathbf{n}T\mathbf{n}} = -\tfrac{1}{3}u, \tag{16.17b}$$

a negative stress which means a pressure. Hence

$$p = \tfrac{1}{3}u \tag{16.18}$$

as in (16.16).

17. UNITS AND UNITS

Some Philosophy

The chapter of units in electromagnetism is a sad chapter, in the author's opinion. How can the brilliance and clarity of the metric system as invented nearly 200 years ago have been mixed up with so many useless details by physicists and technologists during the last 100 years?

There seems to have been no inconvenience in using the Gaussian system in studying the basic laws of electricity and electromagnetism from the very beginning up to the present day's requirements in atomic theory and field theories. Difficulties arise only in a limited field of science, the application of the theory in electromagnetic technology.

Scientists advocating a single system of units believe they have found the final and right solution, if not the absolutely ideal system, in the mks or Giorgi system. According to a well-known book on electromagnetic theory of about 20 years ago: "At all events, it (the mks system) is a good system, easily learned, and one that avoids endless confusion in practical applications. At the moment there appears to be no doubt of its universal adoption in near future."

Next consider a book from a wider field, namely, that of the more general basic topics of theoretical physics appearing 20 years later: "Ich bekenne mich wohl zu dem Grundsatz, dass die Wahl der Einheiten eine reine Angelegenheit der Zweckmassigkeit ist, und dass es sinnlos ist, eine Pseudo-philosophie darauf gründen zu wollen. In verschiedenen Bereichen der Physik und ihrer Anvendungen muss aber nicht immer das Gleiche zweck-mässig sein, ... Ebenso erschien es sinnvoll, das elektrostatische Messystem anzuwenden, da im Bereich atomarer Gebilde von allen elektromagnetischen Grundphenomenen *die Coulombsche Wechselwirkung die stärkste ordnende Kraft besitzt.**"

The necessity of constructing a practical system of units in the early days of technological electrodynamics to complete and partly improve the already existing technical system of units should not be questioned. It probably is also out of the question to modify the accepted mks technical system in any direction to reconcile it somewhat better with the scientific system of units.

Nevertheless, there is no reason why mistakes committed in the distant or near past should not be corrected.

Among them I do not include the refusal of the Heaviside units so highly regretted by numerous scientists. After all, the factor 4π is the surface of the unit sphere just as 2π, so often avoided by replacing the true frequency by $\omega = 2\pi\nu$, is the length of the unit circle.

The first mistake, in this author's opinion, was the division of the electro-magnetic current unit by 10 to obtain the ampere. Imagine the early days with solemn assemblies of scientists making decisions of units for the future

* Emphasis added by the author. A translation of this passage follows: "I profess the maxim that the choice of units is a pure matter of convenience and that it has no sense to base any pseudo-philosophy thereupon. However, in the various branches of physics and its applications the same must not always be the most suitable to the purpose, ... Similarly it appeared appropriate to apply the electrostatic system of units because in the realm of atomic developments among all basic phenomena of electromagnetism *the Coulomb interaction possesses the strongest ordering power.*"

on the basis of their still primitive measuring equipments covering only a scale of a few powers of 10. Were they really justified in setting aside simple laws to replace the electromagnetic units of charge and current by the coulomb and ampere simply for the sake of saving a factor of convenience of only one-tenth?

The following history of units presents several similar cases in adopting precision measurements (believed to be unsurpassable) for a general basis of units rather than stay close to theory and the general laws of nature. Fortunately, by the later discovery of serious fallacies in the basic measurements it was possible to redefine the units.

There evidently is much to learn from the history of the past, and even the advocates of the modern Giorgi system from the last decades might well have been wise in saying: "Let us wait and see."

Admitted that a better and more consistent system of technical units was urgently needed and also that the freedom of choice was very limited. But is it unjustified to ask: Was there a choice at all? Was it inevitable to rule out for all future the possibility of using the Coulomb law in its original form in the new system by enforcing a factor $\sqrt{10}$ into the usual electrostatic definition of charge? Was it inevitable to leave the psychologically well-founded basis of the metric system that the unit of mass density should be that of water?

Consider the new unit of force with the appealing name of newton. It is a force frequently used when weighing a portion of candy. Take the thousand times stronger force and it is of the order of magnitude of a horse's burden. The unit of power would not be very far from a horsepower; more accurately it would have been the most frequently used technical unit, the kilowatt.

The necessary change in electromagnetic units for these amendments, so typical in design for technical needs, would have required not too heavy reforms of electromagnetic units. By retaining the ampere and the coulomb the fundamental change of the basic units appears to have been that of the volt and the watt into the kilovolt and the kilowatt.

What would then have been the units of electrostatic charge, current, and voltage in the MTS system (T for ton)? The units of charge and current would have increased by a factor of one million into 1/3000 of a coulomb and 1/3000 of an ampere. The electrostatic unit of voltage would have been 3000 kilovolt = 3 MeV instead of 300 volts. Today these units may well compete in importance with the former units of low voltage electrotechniques.

Dimension of Units and Conversion Tables

Whatever may be the benefits or the insufficiencies of our systems of units, they are there and they will probably be there for a long time to come. We need not concern ourselves about the habits of more advanced specialists of

Table 2-1. Dimensions of cgs units.

Physical Quantities	Symbol	Gaussian Electrostatic Units	Electromagnetic Units
Length	l	centimeter (cm)	centimeter (cm)
Mass	m	gram (g)	gram (g)
Time	t	second (sec)	second (sec)
Force	F	ml/t^2	ml/t^2
Work, energy	W, U	ml^2/t^2	ml^2/t^2
Power	P	ml^2/t^3	ml^2/t^3
Charge	q, e	$m^{1/2}l^{3/2}/t$	$m^{1/2}l^{1/2}$
Current	J	$m^{1/2}l^{3/2}/t^2$	$m^{1/2}l^{1/2}/t$
Charge density	ρ	$m^{1/2}/l^{3/2}t$	$m^{1/2}/l^{5/2}$
Current density	j	$m^{1/2}/l^{3/2}t^2$	$m^{1/2}/l^{5/2}t$
Electric field	E	$m^{1/2}/l^{1/2}t$	$m^{1/2}l^{1/2}/t^2$
Displacement	D	$m^{1/2}/l^{1/2}t$	$m^{1/2}/l^{3/2}$
Magnetic field Induction	H, B	$m^{1/2}/l^{1/2}t$	$m^{1/2}/l^{1/2}t$
Electric potential Voltage	Φ, V	$m^{1/2}l^{1/2}/t$	$m^{1/2}l^{3/2}/t^2$
Magnetic potential	Φ_m	$m^{1/2}l^{1/2}/t$	$m^{1/2}l^{3/2}/t^2$
Magnetic moment	m	$m^{1/2}l^{5/2}/t$	$m^{1/2}l^{5/2}/t$
Capacity	C	l	t^2/l
Inductance	L	t^2/l	l
Resistance	$R, \omega L$ $1/\omega C$	t/l	l/t

choosing natural units like $\hbar$, c, e, and so forth, for fundamental units, which increases the number of our unit systems. At an appropriate time in their studies all students need to become acquainted with the conversion of units from one to the other of the two main systems: the centimeter-gram-second (cgs) and the meter-kilogram-second (mks) systems.

We first prepare a table of the cgs-system, including both Gaussian or electrostatic and electromagnetic units.

Absolute Measurements

The so-called international electromagnetic standards were made possible by the unforeseen rapid improvement of absolute measurements. To the absolutely measurable quantities we shall also count the velocity of light, the determination of which for a long time lacked the highest degree of precision measurement. Today the situation has changed so that we may feel justified

Table 2-2. Conversion from the mks to the cgs System.

Physical Quantities	Symbol	mks Units	Gaussian Units
Length	l	meter (m)	10^2 cm
Mass	m	kilogram (kg)	10^3 g
Time	t	second (sec)	1 sec
Force	F	newton (N)	10^5 dyne (dyn)
Work energy	W, U	joule (J)	10^7 erg
Power	P	watt (W)	10^7 erg/sec
Charge	q, e	coulomb (C)	$3 \cdot 10^9$ statcoulomb
Current	J	ampere (A)	$3 \cdot 10^9$ statampere
Charge density	ρ	C/m^3	$3 \cdot 10^3$ statcoulomb/cm^3
Current density	j	A/m^2	$3 \cdot 10^5$ statampere/cm^2
Electric field	E	volt/m	$\frac{1}{3} \cdot 10^{-4}$ statvolt/cm
Displacement	D	C/m^3	$12\pi \cdot 10^5$ statvolt/cm (statcoulomb/cm^2)
Magnetic field	H	A-turn/m	$4\pi \cdot 10^{-3}$ oersted (Oe)
Magnetic induction	B	weber/m^2 (Wb/m^2)	10^4 gauss (G)
Electric potential / Voltage	Φ, V	volt (V)	$\frac{1}{3} \cdot 10^{-2}$ statvolt
Capacity	C	farad (F)	$9 \cdot 10^{11}$ cm
Inductance	L	henry (H)	$\frac{1}{9} \cdot 10^{-11}$ sec^2/cm
Resistance	R, ωL, $1/\omega C$	ohm (Ω)	$\frac{1}{9} \cdot 10^{-11}$ sec/cm
Magnetic flux	Φ	weber (Wb)	10^8 gauss/cm^2 (maxwell) or Mx

in considering the former difference between electrostatic and electromagnetic units removed. The already-mentioned electrostatic measurement of voltage may therefore be thought of as the determination of the electromagnetic voltage as well.

Among other possibilities we shall only briefly mention the standards of current and resistance. The design for measuring currents in absolute standard is fairly similar to the electricity balance, the actual measurement being that of a mechanical force on a coil by means of an ordinary but highly sensitive balance. The coil of radius b is placed between two larger coils of radius $a > b$, so that it is comparatively easy to evaluate the field in the space between them which acts on the smaller coil.

The three coils, all of them in series, carry the same current that is to be measured. In the two larger coils, however, it is flowing in opposite directions

so as to produce the attraction of the smaller coil by one and repulsion by the other of the larger coils. The smaller coil is fixed to the balance which measures the force upon it: The force is proportional to the square current. A simultaneous passage of the current through a silver voltameter provides the necessary comparison with this more practical standard instrument.

Even simpler is the principle for measuring resistance in absolute electromagnetic units of the dimension of a velocity. In principle the device consists of a solenoid in whose interior a circular metallic desk is rotating with an angular velocity ω, with its center on the solenoid axis. In the solenoid a current from a galvanic element is flowing, and simultaneously also through the resistance R which is to be measured. From either end of the resistance a connection is produced through a galvanometer used as a zero instrument. The other passage of the connection is from the axis to the periphery of the circular desk.

In electromagnetic units the induction field in the vacuum is

$$B = 4\pi Jn, \qquad (n = \text{turns/cm}). \tag{17.1}$$

Owing to the rotation of the desk the metallic electrons are carried along with the velocity $r\omega$ perpendicular to the induction field with the effect of a Lorentz electric field

$$r\omega B = 4\pi Jnr\omega. \tag{17.2}$$

The potential difference or electromotive force between the axis and periphery hence becomes

$$E = 4\pi Jn\omega \int_0^b r\, dr = 2\pi Jn\omega b^2. \tag{17.3}$$

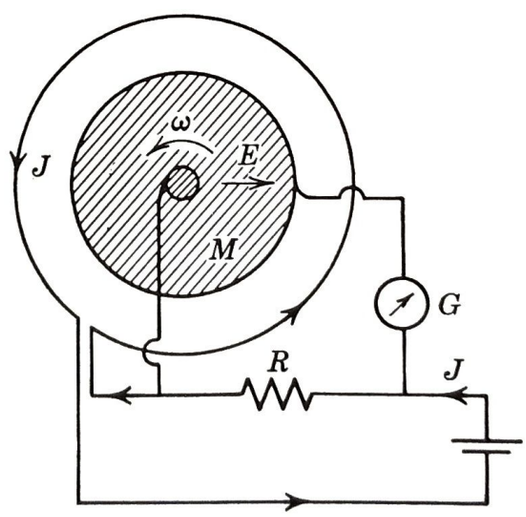

Fig. 2-8. Device for the absolute measurement of resistances. Lorentz forces in the rotating metallic cylinder in the magnetic field of a solenoid set up a potential difference between the center and the circumference of the cylinder. It is compared with the voltage through the unknown resistance R set up by the solenoid current through the resistance. This is the L. Lorentz method.

In the case of zero current the expression equals RJ. Hence the resistance

$$R = 2\pi n\omega b^2 \tag{17.4}$$

as expressed in the electromagnetic resistance unit, which is seen to be a velocity ($n = \text{cm}^{-1}$). (See Fig. 2-8.)

If we question the real sense of dimensions of electromagnetic units as expressed in fractional powers of mechanical units, the nature of absolute measurements is apt to give us the answer to the question. The measured mechanical quantities are never related directly to charge, current, or field strength. They are always related to second-degree quantities such as squares of quantities like charge, current, and field strength, or to products of such quantities.

CHAPTER 3

Electromagnetic Radiation

18. STRUCTURE OF ELECTROMAGNETIC WAVES

Fundamental Equations

Having discussed the various fundamental discoveries of electric and magnetic phenomena and having expressed the results in general laws, we have reached a set of differential equations known as Maxwell's electromagnetic equations.

Conversely, all the experiences and statements on which our final equations are based, whether in the form of elementary laws of force or integral principles, are easily derived from the full set of fundamental differential equations.

The quantities used for expressing the differential laws of electrodynamics are the field variables **E**, **D**, **H**, **B** together with the charge and current densities ρ and $\mathbf{j} = \rho\mathbf{v}$, all of them considered functions of space and time coordinates x, y, z, t. In addition there are the material constants ε and μ connecting pairs of field variables, **D** with **E** and **B** with **H**, and hence in reality reducing the number of field variables. We also have material constants like the conductivity σ connecting the current density with the electric field, $\mathbf{j} = \sigma\mathbf{E}$.

The connection between the field vectors is given by

$$\mathbf{D} = \varepsilon\mathbf{E}, \qquad \mathbf{B} = \mu\mathbf{H}. \tag{18.1}$$

Next come the differential equations from electrostatics and magnetostatics

$$\operatorname{div}\mathbf{D} = 4\pi\rho, \qquad \operatorname{div}\mathbf{B} = 0. \tag{18.2}$$

The electromagnetic equations in the proper sense, connecting electric and magnetic field quantities, are the differential Ampère law in its most general form, including Maxwell's displacement current

$$\operatorname{curl}\mathbf{H} = \frac{1}{c}\frac{\partial\mathbf{D}}{\partial t} + \frac{4\pi}{c}\mathbf{j}, \tag{18.3}$$

and finally the differential form of Faraday's induction law,

$$\operatorname{curl} \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}. \tag{18.4}$$

It should be noted that the quantities ρ and $\mathbf{j}$ are not mutually independent but connected by the law

$$\operatorname{div} \mathbf{j} + \frac{\partial \rho}{\partial t} = 0, \tag{18.5}$$

expressing the conservation of charge. Furthermore, adopting the expression

$$u = \frac{1}{8\pi}(\mathbf{ED} + \mathbf{HB}), \tag{18.6}$$

we find that the principle of conservation of energy leads to the interpretation of

$$\mathbf{S} = \frac{c}{4\pi}\mathbf{E} \times \mathbf{H} \tag{18.7}$$

as an energy current called Poynting's or the radiation vector.

The force acting per unit volume

$$\mathbf{F} = \rho\mathbf{E} + \frac{1}{c}\mathbf{j} \times \mathbf{B} \tag{18.8}$$

comprises the familiar electrostatic force, together with the interaction of charges in motion with the magnetic field. The volume forces can be transformed so as to become interpretable as surface forces acting directly between neighboring regions through separating surfaces. These forces can be expressed by means of the generalized Maxwell stress tensor

$$T = \frac{1}{8\pi}[\mathbf{E} \cdot \mathbf{D} + \mathbf{H} \cdot \mathbf{B} - I(\mathbf{ED} + \mathbf{HB})]. \tag{18.9}$$

From the law of conservation of momentum it follows that

$$\mathbf{g} = \frac{1}{4\pi c}(\mathbf{D} \times \mathbf{B}) = \frac{1}{v^2}\mathbf{S} \tag{18.10}$$

is the momentum density current.

Electromagnetic Potentials

In electrostatics and magnetostatics we experienced the convenience of relating field quantities to potential functions. The electrostatic potential and the electromagnetic vector potential may be taken directly over into radiation

theory simply under the names of scalar and vector potentials. Their usefulness is so evident that it should be emphasized at the beginning of our studies of electromagnetic waves.

We first write in accordance with (18.2)

$$\mathbf{B} = \operatorname{curl} \mathbf{A} \tag{18.11}$$

with $\mathbf{A}$ the vector potential. From (18.4) written as

$$\operatorname{curl}\left(\mathbf{E} + \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}\right) = 0 \tag{18.11a}$$

it follows that

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} - \nabla\Phi, \tag{18.12}$$

where Φ is now the scalar potential to be identified with the electrostatic potential in static problems.

In homogeneous matter with constant ε and μ we have from (18.2) and (18.3)

$$-\frac{\varepsilon}{c}\frac{\partial}{\partial t}\operatorname{div}\mathbf{A} - \varepsilon\nabla^2\Phi = 4\pi\rho, \tag{18.12a}$$

$$\frac{1}{\mu}\operatorname{curl}\operatorname{curl}\mathbf{A} = -\frac{\varepsilon}{c^2}\frac{\partial^2 \mathbf{A}}{\partial t^2} - \frac{1}{c}\frac{\partial}{\partial t}\nabla\Phi + \frac{4\pi}{c}\mathbf{j}. \tag{18.12b}$$

With

$$\operatorname{div}\mathbf{A} + \frac{\varepsilon\mu}{c}\frac{\partial\Phi}{\partial t} = \Delta, \tag{18.13}$$

using

$$\operatorname{curl}\operatorname{curl}\mathbf{A} = \nabla\operatorname{div}\mathbf{A} - \nabla^2\mathbf{A}, \tag{18.13a}$$

the equations become

$$\nabla^2\Phi - \frac{\varepsilon\mu}{c^2}\frac{\partial^2\Phi}{\partial t^2} = -\frac{4\pi}{\varepsilon}\rho - \frac{1}{c}\frac{\partial\Delta}{\partial t}, \tag{18.14}$$

$$\nabla^2\mathbf{A} - \frac{\varepsilon\mu}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = -\frac{4\pi\mu}{c}\mathbf{j} + V\Delta. \tag{18.15}$$

The potentials $\mathbf{A}$ and Φ are not unique. If $\mathbf{A}'$ and Φ' are potentials giving $\Delta \neq 0$, we may replace them by

$$\mathbf{A}' = \mathbf{A} + \nabla\psi, \qquad \Phi' = \Phi - \frac{1}{c}\frac{\partial\psi}{\partial t} \tag{18.16}$$

which is called a gauge transformation. This gives

$$\Delta = \operatorname{div}\mathbf{A} + \frac{\varepsilon\mu}{c}\frac{\partial\Phi}{\partial t} + \left(\nabla^2 - \frac{\varepsilon\mu}{c^2}\frac{\partial^2}{\partial t^2}\right)\psi, \tag{18.16a}$$

so that if ψ is chosen so as to obey the equation

$$\nabla^2\psi - \frac{\varepsilon\mu}{c^2}\frac{\partial^2\psi}{\partial t^2} = \Delta, \tag{18.16b}$$

our potentials Φ and $\mathbf{A}$ will satisfy the well-known Lorentz condition

$$\operatorname{div}\mathbf{A} + \frac{\varepsilon\mu}{c}\frac{\partial\Phi}{\partial t} = 0, \tag{18.17}$$

that is, $\Delta = 0$. This simplifies (18.14) and (18.15) into the inhomogeneous wave equations

$$\nabla^2\Phi - \frac{\varepsilon\mu}{c^2}\frac{\partial^2\Phi}{\partial t^2} = -\frac{4\pi}{\varepsilon}\rho, \tag{18.17a}$$

$$\nabla^2\mathbf{A} - \frac{\varepsilon\mu}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = -\frac{4\pi\mu}{c}\mathbf{j}. \tag{18.17b}$$

Free Plane Electromagnetic Waves

Consider electromagnetic waves in charge-free space $\rho = 0$, $\mathbf{j} = 0$; the scalar potential equation becomes

$$\nabla^2\Phi - \frac{1}{v^2}\frac{\partial^2\Phi}{\partial t^2} = 0, \qquad v = \frac{c}{\sqrt{\varepsilon\mu}}. \tag{18.18}$$

The simplest solutions of the equation are those representing plane waves, of which we obtain a particular one on considering solutions that depend on only one coordinate x, that is, solutions of the equation

$$\left(\frac{\partial^2}{\partial x^2} - \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\right)\Phi = 0. \tag{18.19}$$

The general solution is easily found to be

$$\Phi = \Phi(x \pm vt), \tag{18.19a}$$

the plus sign denoting a wave traveling with the velocity v in the direction of the negative x-axis. On turning to waves traveling in arbitrary directions, as indicated by a unit vector $\mathbf{s}$ (rather than $\mathbf{n}$ to avoid confusion with the refraction index n), we have no need for the double sign. For arbitrary direction of the plane wave we therefore write

$$\Phi = \Phi(\mathbf{sr} - vt). \tag{18.19b}$$

From the equation

$$\mathbf{sr} - vt = \text{const} \tag{18.19c}$$

we see that the wave function has the same value on a plane perpendicular

to the direction of the wave normal **s** and traveling with the velocity v in the **s**-direction.

In order to satisfy the Lorentz condition we may write

$$\mathbf{A} = \mathbf{A}_0 f(\mathbf{rs} - vt), \qquad \Phi = -\frac{\mathbf{sA}_0}{\varepsilon\mu v} f(\mathbf{rs} - vt). \tag{18.20}$$

On choosing

$$\mathbf{sA} = 0, \tag{18.20a}$$

considering only transversal waves, we have $\Phi = 0$ and hence can dispense with the scalar potential Φ. The Lorentz condition thereby degenerates into $\operatorname{div} \mathbf{A} = 0$. The result also follows from the condition $\operatorname{div} \mathbf{E} = 0$.

The field vectors are obtained using (18.11) and (18.12)

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} = \frac{v}{c}\mathbf{A}_0 f'(\mathbf{rs} - vt), \tag{18.21}$$

$$\mathbf{B} = \operatorname{curl} \mathbf{A} = (\mathbf{s} \times \mathbf{A}_0) f'(\mathbf{rA} - vt). \tag{18.21a}$$

We write the last equation

$$\mathbf{B} = \frac{c}{v}\mathbf{s} \times \mathbf{E} \tag{18.21b}$$

showing that **s**, **E**, and **B** are mutually orthogonal vectors, forming in the above sequence a right-hand coordinate system. Moreover, since

$$\varepsilon\left(\frac{v}{c}\right)^2 = \frac{\varepsilon}{\varepsilon\mu} = \frac{1}{\mu}, \tag{18.21c}$$

we have

$$\mathbf{ED} = \mathbf{HB} = \frac{1}{\mu}\mathbf{A}_0^2 f'^2 \tag{18.22}$$

which means that the energy is equally divided into electric and magnetic field energy. Similarly

$$\mathbf{S} = \frac{c}{4\pi}(\mathbf{E} \times \mathbf{H}) = \frac{\mathbf{v}}{4\pi}\frac{1}{\mu}\mathbf{A}_0^2 f'^2 = \frac{\mathbf{v}}{8\pi}(\mathbf{ED} + \mathbf{HB}) = \mathbf{v}u \tag{18.23}$$

with u the field energy density. Hence the field energy is traveling with the velocity of the wave motion which is easily understood to be the only possible result, since wave structure is unchanged except for its propagation in the direction **s** with velocity v.

Monochromatic Waves and Group Velocity in Dispersive Media

Usually electromagnetic waves have the character of a more or less pronounced periodic process. For a limited period $0 < t < T$ it is well known

that a function of time can be expressed by Fourier series with individual terms of frequencies $\nu = k/T$, $k = 1, 2, \cdots$. For an infinite period of time it is still possible to analyze the function as consisting of terms of definite frequencies. In that case, however, the frequency spectrum becomes continuous and the function is expressible only in the form of a Fourier integral.

In turning to monochromatic solutions of the electromagnetic equations we have to realize that, although ε and μ (and hence the refraction index $n = \sqrt{\varepsilon\mu}$, and velocity $v = c/n$) may be space- and time-independent in the proper sense, these quantities are connected with interior periodic processes that make them depend on the frequency of the monochromatic wave. This phenomenon is called dispersion. Moreover, in order to obtain monochromatic solutions we have to use the properties of the equations of being separable in space and time coordinates. The time-independent parts of the solutions then become pure sine and cosine functions.

For the sake of simplicity we shall replace functions like $\sin \omega t$ and $\cos \omega t$ by exponential functions $\exp(i\omega t)$ or $\exp(-i\omega t)$, having available thereby a double set of solutions, namely, the real and the imaginary parts of the expression. A scalar plane wave then is, for instance,

$$\Phi = \exp\left(i(\mathbf{kr} - \omega t)\right) \tag{18.24}$$

with $\omega = 2\pi\nu$ the angular frequency or, for brevity, simply frequency, and

$$\mathbf{k} = \frac{2\pi}{\lambda}\,\mathbf{s} \tag{18.24a}$$

the angular wave number vector, or simply wave vector. The relation between frequency and angular wave number is

$$\frac{\omega}{k} = v = \frac{c}{\sqrt{\varepsilon\mu}}\,. \tag{18.24b}$$

Hence the scalar plane wave also is

$$\omega = \exp\left[i\left(\frac{\mathbf{sr}}{v - \omega t}\right)\right]. \tag{18.25}$$

In monochromatic waves the velocity of propagation is called the phase velocity. In dispersive media, as already explained, the phase velocity will depend on the frequency. In that case the phase velocity is no more the traveling speed of an electromagnetic disturbance or energy impulse, the velocity of signals, even if the wave motion is confined to a narrow region of frequencies. The signal velocity corresponds to what is called the group velocity g which may be obtained as follows.

Consider a plane wave with the wave normal in the x-direction,

$$\Phi = \exp\,[i(kx - \omega t)]. \tag{18.26}$$

To this we add another wave of slightly different frequency and wave number and, for simplicity, the same amplitude. The composite wave becomes

$$\begin{aligned}\Phi &= \exp\,[i(kx - \omega t)] \times \exp\,\{i[(k + \Delta k)x - (\omega + \Delta\omega)t]\} \\ &= \exp\,i[(k + \tfrac{1}{2}\Delta k)x - (\omega + \tfrac{1}{2}\Delta\omega)t] \cdot 2\cos\tfrac{1}{2}(x\,\Delta k - t\,\Delta\omega).\end{aligned} \tag{18.27}$$

For very small $\Delta\omega$ the result is a wave of almost unaltered frequency and phase velocity, however, with a variable amplitude that is traveling with a different speed, the group velocity g, which for a given mean frequency ω may be uniquely defined as

$$g = \lim_{\Delta\omega \to 0} \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk}. \tag{18.28}$$

Putting $\omega = kv$, we may also write

$$g = v + k\frac{dv}{dk}. \tag{18.28a}$$

From this it is seen that group and phase velocity are equal only in the case of frequency-independent phase velocity, that is, no dispersion.

According to relativity theory no energy impulse, no signal, can travel with higher speed than the velocity of light. Hence if by some anomalous refraction index $n < 1$ the phase velocity should exceed the velocity of light, the additional term in (18.28a) has to provide for keeping $g < c$.

In the case of normal refraction and normal dispersion with n increasing and v decreasing with ω and k, the group velocity g is smaller than the phase velocity v. Cases of abnormal dispersion usually require refined theoretical investigations, and simple results with respect to the behavior of the group velocity can scarcely be drawn directly from (18.28a). (See also Fig. 3-1.)

19. THE HERTZ METHOD OF SOLUTION

The Charge Displacement Vector or Charge Transport

The continuity equation for the conservation of charge connecting the spatial variation of the current and the time variation of the charge reveals the possibility of expressing both quantities by means of the same vector field $\mathbf{p}$ on writing

$$\rho = -\text{div}\,\mathbf{p}, \qquad j = \frac{\partial \mathbf{p}}{\partial t}, \tag{19.1}$$

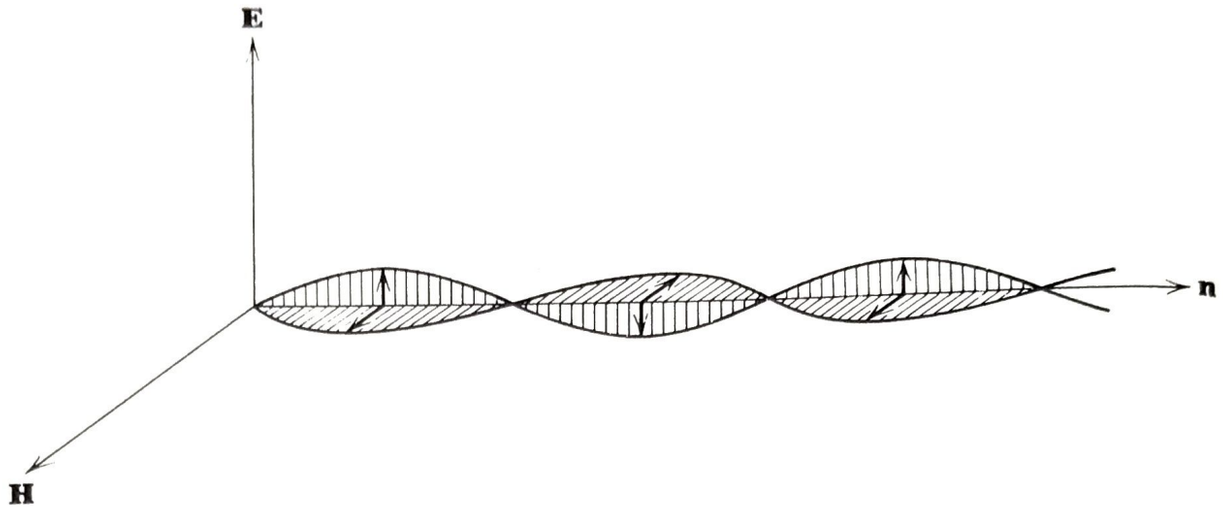

Fig. 3-1. A plane electromagnetic wave.

in agreement with $\operatorname{div} \mathbf{j} + \partial\rho/\partial t = 0$. The Lorentz convention expression (18.17) being of a similar form, it follows that we may proceed in the same way to find the potentials, writing

$$\Phi = -\frac{1}{\varepsilon} \operatorname{div} \mathbf{Z}, \qquad \mathbf{A} = \frac{\mu}{c} \frac{\partial \mathbf{Z}}{\partial t}. \tag{19.2}$$

The vector $\mathbf{Z}$ as introduced in electromagnetic theory by Heinrich Hertz is called the Hertz vector. With the definition (19.2) it obeys the inhomogeneous wave equation

$$\left(\nabla^2 - \frac{\varepsilon\mu}{c^2} \frac{\partial^2}{\partial t^2}\right) \mathbf{Z} = -4\pi \mathbf{p}. \tag{19.3}$$

The vector field $\mathbf{p}(\mathbf{r}, t)$ is very closely related to the polarization field $\mathbf{P}$ in electrostatics. Its dimension is the charge density times the length; it represents therefore a displacement of charge density or charge density transport. Whereas $\mathbf{P}$, however, is only a sum of microscopic displacements of charges within atoms or molecules, $\mathbf{p}$ represents a true macroscopic motion of freely movable charges.

The Hertz Vector for Plane Waves

For plane waves the Hertz vector is not particularly needed. We therefore only mention quite briefly that if taken in the form of a transverse wave

$$\mathbf{Z} = \mathbf{Z}_0 f(\mathbf{kr} - \omega t), \qquad \mathbf{kZ}_0 = 0, \tag{19.4}$$

the scalar potential $\Phi = (1/\varepsilon) \operatorname{div} \mathbf{Z}$ vanishes automatically in accordance with (18.20) and (18.21).

Spherical Solutions. The Hertz Dipole

We still consider only the homogeneous equations for free waves, however, now of the spherical type, that is, expressible in spherical polar coordinates r, ϑ, Φ. The homogeneous wave equation for $\mathbf{Z}$ is written

$$\left(\nabla^2 - \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{Z} = 0, \qquad v = \frac{c}{\sqrt{\varepsilon\mu}}, \tag{19.5}$$

and is separable in t and space coordinates. If the time factor is, say, $\exp(i\omega t)$, the equation becomes

$$(\nabla^2 + k^2)\mathbf{Z} = 0, \qquad k = \frac{\omega}{v}. \tag{19.5a}$$

It has an infinity of solutions corresponding to angular wave functions $Y_1^m = P_1^m(\cos\vartheta)\exp(\mathrm{im}\,\Phi)$. At this stage we shall not look for the most general solutions, since the simplest spherically symmetric solutions for the Hertz vector already provide a great number of valuable details.

Taking $\mathbf{Z}$ to depend only on r and t, we may write (19.5)

$$\left(\frac{\partial^2}{\partial r^2} - \frac{1}{v^2}\frac{\partial^2}{\partial t^2}\right)r\mathbf{Z} = 0, \tag{19.6}$$

whose general solution we prefer to write in the form

$$\mathbf{Z} = \frac{1}{r}\mathbf{p}\left(t - \frac{r}{v}\right), \tag{19.7}$$

where $p_x(t)$, $p_y(t)$, $p_z(t)$ are independent functions of time. A little more specialized is the vector

$$\mathbf{Z} = \frac{1}{r}\mathbf{Z}_0 f\left(t - \frac{r}{v}\right) \tag{19.7a}$$

with $\mathbf{Z}_0$ a constant vector; hence the direction of $\mathbf{Z}$ is given. This form will also usually serve the purpose, but the more general form (19.7) provides more compact formulas.

For instance, calculating the electromagnetic potential according to (19.2), on removing the argument $t - r/c$, we obtain

$$\mathbf{A} = \frac{\mu}{c}\frac{\dot{\mathbf{p}}}{r}, \qquad \Phi = \frac{\mathbf{rp}}{\varepsilon r^3} + \frac{\mathbf{r}\dot{\mathbf{p}}}{\varepsilon v r^2}. \tag{19.8}$$

Inspecting the scalar potential for very small r-values, the second term of Φ is small in comparison with the first. Next the argument $t - r/c$ may with considerable accuracy be replaced simply by t. Then Φ becomes the electrostatic potential of an electric dipole $\mathbf{p}(t)$ which, in contrast to the electrostatic dipole, varies with time.

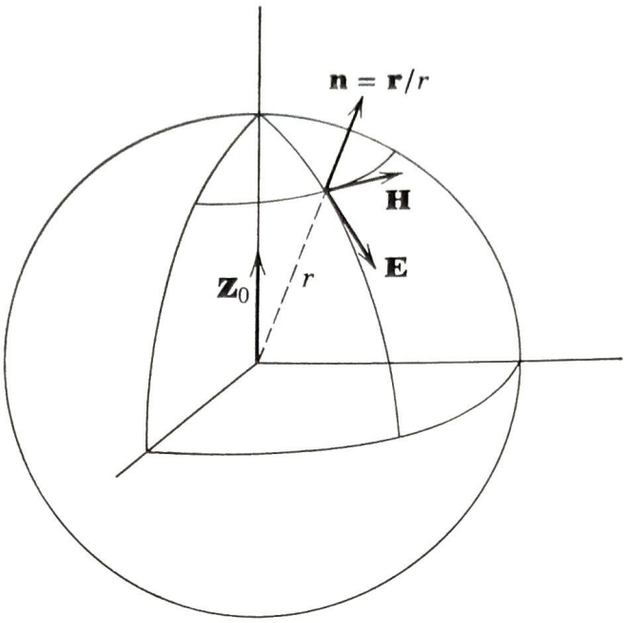

Fig. 3-2. A spherical electromagnetic wave.

This means that the spherical electromagnetic waves to be discussed here are not free waves in the same sense as the free plane waves. The whole radiation field has a singularity or discontinuity at the center of the waves, and this center conceals the source of the field. (See Fig. 3-2.) We conclude that in the wave center is imbedded a true dipole of direction and shape $\mathbf{p}(t)$ varying with time; this is the Hertz dipole. Similarly writing $\mathbf{p} = e\mathbf{q}$, $\dot{\mathbf{p}} = e\dot{\mathbf{p}} = e\mathbf{v}$, $\mathbf{A}$ corresponds to the vector potential of a point charge moving with the velocity $\mathbf{v}$.

In the next step we calculate the electric and magnetic field vector, for instance

$$\mathbf{H} = \frac{1}{\mu} \operatorname{curl} \mathbf{A} = \left(\frac{1}{c} \frac{\dot{\mathbf{p}}}{r^2} + \frac{\dot{\mathbf{p}}}{cvr} \right) \times \frac{\mathbf{r}}{r}. \tag{19.9}$$

To evaluate $\mathbf{E}$ we note that from the definition (18.12) as applied to (19.2) we have

$$\mathbf{E} = \frac{1}{\varepsilon} \left(\nabla \operatorname{div} \mathbf{Z} - \frac{\varepsilon\mu}{c^2} \frac{\partial^2 \mathbf{Z}}{\partial t^2} \right). \tag{19.10}$$

Here the second term is extremely simple. Nevertheless with the complexity of the first term we shall prefer to replace it by $\nabla^2 \mathbf{Z}$ from (19.5) and write

$$\mathbf{E} = \frac{1}{\varepsilon} \operatorname{curl} \operatorname{curl} \mathbf{Z}. \tag{19.10a}$$

Similarly to (19.9) we have

$$\operatorname{curl} \mathbf{Z} = \left(\frac{\mathbf{p}}{r^3} + \frac{\ddot{\mathbf{p}}}{vr^2} \right) \times \mathbf{r}. \tag{19.10b}$$

Here we must be aware of the formula

$$\operatorname{curl}(\mathbf{p} \times \mathbf{r}) = 2\mathbf{p} + \frac{1}{vr}(\dot{\mathbf{p}} \times \mathbf{r}) \times \mathbf{r} \tag{19.10c}$$

and the corresponding formula for curl $(\dot{\mathbf{p}} \times \mathbf{r})$. This gives fairly easily

$$\operatorname{curl}\operatorname{curl}\mathbf{Z} = \frac{2\mathbf{p}}{r^3} + \frac{2\dot{\mathbf{p}}}{vr^2} + \left[\left(\frac{\dot{\mathbf{p}}}{vr^4} + \frac{\ddot{\mathbf{p}}}{v^2r^3}\right) \times \mathbf{r}\right] \times \mathbf{r} + \nabla\frac{1}{r^3} \times (\mathbf{p} \times \mathbf{r}) + \nabla\frac{1}{vr^2} \times (\dot{\mathbf{p}} \times \mathbf{r}). \tag{19.10d}$$

Finally

$$\mathbf{D} = \varepsilon\mathbf{E} = \frac{2\mathbf{p}}{r^3} + \frac{2\dot{\mathbf{p}}}{vr^2} + \left[\left(\frac{3\mathbf{p}}{r^3} + \frac{3\dot{\mathbf{p}}}{vr^2} + \frac{\ddot{\mathbf{p}}}{v^2r}\right) \times \frac{\mathbf{r}}{r}\right] \times \frac{\mathbf{r}}{r}. \tag{19.11}$$

Admittedly the last formula is fairly complex. On the other hand, it keeps strict account with the wave motion in the entire region of radiation. The terms containing only $\mathbf{p}$ show an electrostatic field, those containing $\dot{\mathbf{p}}$ a quasistationary field. Finally, the last and simplest term containing $\ddot{\mathbf{p}}$ is the only one representing true radiation in the sense of radiative energy leaving the radiation center. This naturally divides the space surrounding the field source into three characteristic regions which will be called the static zone, the induction zone, and the radiation zone to replace the less distinctive characteristics of near, intermediate, and distant or wave zone.

The expression for $\mathbf{H}$ may also be discussed. However, owing to the lack of $\mathbf{p}$, there is nothing similar to a static field; the part depending on $\dot{\mathbf{p}}$ is easily understood as similar to a quasistationary electromagnetic field. The radiative part depending on $\ddot{\mathbf{p}}$ is simple as the radiative part of the electric field.

On going from small to large distances from the radiation center, the radiative parts of the field become more and more pronounced, and the distant regions where the rest of the fields may be neglected in comparison are called the radiation zone. In this region we therefore write

$$\mathbf{H} = \frac{\ddot{\mathbf{p}}}{cvr} \times \frac{\mathbf{r}}{r}, \qquad \mathbf{E} = \frac{c}{\varepsilon v}\mathbf{H} \times \frac{\mathbf{r}}{r}. \tag{19.12}$$

Again we note that the three vectors $\mathbf{r}^0 = \mathbf{r}/r$, $\mathbf{E}$, and $\mathbf{H}$ are mutually orthogonal and form a right-hand coordinate system. Squaring $\mathbf{E}$, we find that

$$\varepsilon\mathbf{E}^2 = \mu\mathbf{H}^2. \tag{19.13}$$

So again the energy is equally divided into electric and magnetic field energy.

Dipole Radiation

The phase velocity of radial waves is the same as that of free plane waves. To find the energy transport of the wave we need consider only the wave

zone values of the field vectors as given in (19.12). The Poynting vector becomes

$$\mathbf{S} = \frac{c}{4\pi}\,\mathbf{E} \times \mathbf{H} = \frac{c^2}{4\pi\varepsilon v}\,\mathbf{H}^2\mathbf{r}^0. \tag{19.14}$$

We now assume a definite direction of $\mathbf{Z}$ or $\mathbf{p}$ as explained in (19.7*a*) and take this direction for z-axis with polar angle coordinates ϑ and φ for the radius vector $\mathbf{r}$ or the wave normal $\mathbf{r}^0 = \mathbf{r}/r$. This gives

$$\mathbf{H}^2 = \frac{\ddot{\mathbf{p}}^2}{c^2 v^2 r^2}\sin^2\vartheta \tag{19.14a}$$

and

$$\mathbf{S} = \frac{1}{4\pi r^2}\cdot\frac{\ddot{\mathbf{p}}^2\sin^2\vartheta}{\varepsilon v^3}\frac{\mathbf{r}}{r}. \tag{19.14b}$$

The energy loss per unit time through a spherical surface, $d\boldsymbol{\sigma} = \frac{\mathbf{r}}{r}\,r^2\sin\vartheta\,d\vartheta\,d\Phi$, becomes

$$\eta_e = \int \mathbf{S}\,d\boldsymbol{\sigma} = \frac{2}{3}\frac{\ddot{\mathbf{p}}^2}{\varepsilon v^3}. \tag{19.15}$$

If $\mathbf{p}(t)$ is an oscillating dipole

$$\mathbf{p} = \mathbf{p}_0 \sin\omega\left(t - \frac{r}{v}\right), \tag{19.15a}$$

the rate of emitted radiation becomes

$$\eta_e = \frac{2}{3}\frac{\omega^4}{\varepsilon v^3}\,\mathbf{p}_0{}^2\sin^2\omega\left(t - \frac{r}{v}\right). \tag{19.15b}$$

Finally we may find the time average of emission. Assuming

$$\mathbf{p}_0 = e\mathbf{q}_0, \tag{19.16}$$

for simplicity we put $\varepsilon = \mu = 1$ and $v = c$ to obtain the well-known formula for the rate of radiation from an oscillating charged particle

$$\bar{\eta}_e = \frac{1}{3}\frac{\omega^4 e^2}{c^3}\,\mathbf{q}_0{}^2. \tag{19.16a}$$

20. THE SOLUTION OF INHOMOGENEOUS WAVE EQUATIONS

Intuitive Derivation from Solutions for Point Sources of the Field

Since the material constants ε and μ of previous sections have been treated as constants, they never seriously interfered with the methods of solution.

There will therefore be no loss of generality in putting

$$\varepsilon = \mu = 1 \qquad n = \frac{1}{\sqrt{\varepsilon\mu}} = 1 \qquad v = c. \tag{20.1}$$

The inhomogeneous wave equations for electromagnetic potentials and the Hertz vector then become

$$\nabla^2\Phi - \frac{1}{c^2}\frac{\partial^2\Phi}{\partial t^2} = -4\pi\rho(\mathbf{r}, t), \tag{20.1a}$$

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\frac{\partial^2\mathbf{A}}{\partial t^2} = -\frac{4\pi}{c}\mathbf{j}(\mathbf{r}, t), \tag{20.1b}$$

$$\nabla^2\mathbf{Z} - \frac{1}{c^2}\frac{\partial^2\mathbf{Z}}{\partial t^2} = -4\pi\mathbf{p}(\mathbf{r}, t), \tag{20.1c}$$

with additional equations

$$\operatorname{div}\mathbf{j} + \frac{\partial\rho}{\partial t} = 0, \tag{20.1d}$$

$$\mathbf{j} = \frac{\partial\mathbf{p}}{\partial t}, \qquad \rho = -\operatorname{div}\mathbf{p}, \tag{20.1e}$$

$$\operatorname{div}\mathbf{A} + \frac{1}{c}\frac{\partial\Phi}{\partial t} = 0, \tag{20.1f}$$

$$\mathbf{A} = \frac{1}{c}\frac{\partial\mathbf{Z}}{\partial t}, \qquad \Phi = -\operatorname{div}\mathbf{Z}. \tag{20.1g}$$

On studying the corresponding homogeneous equations and obtaining their solutions in the form of apparently free spherical waves, we realized that they were not in fact free waves, their sources being hidden in the singular point of the waves, the radiation center.

If the source of radiation were characterized by the transport vector $\mathbf{p}(t)$ as a function of time, the resulting Hertz vector would be found to be

$$\mathbf{Z} = \frac{\mathbf{p}(t - r/c)}{r}. \tag{20.2}$$

The essential point is here the replacement of the time argument t by the retarded time

$$t' = t - r/c. \tag{20.3}$$

In the handling of space coordinates, however, it appears that no essentially different point of view is called for when passing from the static Poisson equation to the electromagnetic wave equation. Hence we may be fairly

safe in assuming the solution

$$\mathbf{Z}(\mathbf{r}, t) = \int \frac{\mathbf{p}(\mathbf{r}', t - R/c)}{R}\, d\tau', \tag{20.4}$$

with the convenient abbreviation

$$R = R(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|. \tag{20.4a}$$

The confidence in the equation may be supported by the techniques of delta functions, on writing

$$\mathbf{p}(\mathbf{r}, t) = \int \mathbf{p}(\mathbf{r}', t)\, \delta(\mathbf{r} - \mathbf{r}')\, d\tau' \tag{20.4b}$$

which, however, is scarcely more than an illustration of the intuitive point of view.

Proof of Correctness of the Solution

In some cases, when explaining a method of solution in more detail, we need to apply some general method. It is customary to use the so-called Green's method which, however, has a number of variants depending on the starting point for choosing an adequate Green's function. We therefore prefer to give a more direct proof, which when needed may be transformed into or compared with particular forms of Green's method.

To make the solution brief we choose convenient transformations of independent variables. To this end we might use the two sets x, y, z, t and x', y', z', t', with $(x', y', z') = (x, y, z)$, whereas $t' = t - r/c$ is the retarded time of (20.3). Note, however, that in the following discussion we shall use $\mathbf{r}$ and $\mathbf{r}'$ in quite different meanings, namely, as the different coordinates of a field point and the field source.

To avoid confusion we therefore first introduce a second set of variables under the names of ξ, η, ζ, τ, or briefly $\boldsymbol{\rho}, \tau$. Next for the general scalar wave equation we write

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\Psi(\mathbf{r}, t) = -4\pi f(\mathbf{r}, t), \tag{20.5}$$

rather than use $\Phi(\mathbf{r}, t)$ and $\rho(\mathbf{r}, t)$ from the scalar potential, in order to stress the general character of the problem.

We now consider the transformation

$$\mathbf{r} = \boldsymbol{\rho} \qquad t = \tau + \frac{R}{c}, \tag{20.6}$$

where

$$R = |\mathbf{R}|, \qquad \mathbf{R} = \mathbf{r} - \mathbf{r}_0 = \boldsymbol{\rho} - \mathbf{r}_0, \tag{20.6a}$$

hence R is the source point distance from a fixed point $\mathbf{r}_0$ which may be taken to be the field point.

As expressed in the new coordinates the wave equation at retarded time $\tau = t - R/c$ reads

$$\left(\nabla_\rho^2 - \frac{1}{c^2}\frac{\partial^2}{\partial \tau^2}\right)\Psi\left(\mathbf{r}, t - \frac{R}{c}\right) = -4\pi f\left(\mathbf{r}, t - \frac{R}{c}\right). \tag{20.7}$$

Using the transformation (20.6), we find

$$\nabla_\rho = \nabla + \frac{\mathbf{R}}{R}\frac{1}{c}\frac{\partial}{\partial t},$$

$$\nabla_\rho^2 = \nabla^2 + \frac{2}{R}\frac{1}{c}\frac{\partial t}{\partial t} + 2\frac{\mathbf{R}}{R^2}\nabla\frac{1}{c}\frac{\partial}{\partial t} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2},$$

$$= R\,\mathrm{div}\left[\frac{1}{R}\nabla - \left(\nabla\frac{1}{R}\right) + \frac{2\mathbf{R}}{R^2}\frac{1}{c}\frac{\partial}{\partial t}\right] + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}, \tag{20.7a}$$

on observing that $\nabla^2(1/R) = 0$, and hence

$$\frac{1}{R}\nabla^2 = \mathrm{div}\left[\frac{1}{R}\nabla - \left(\nabla\frac{1}{R}\right)\right]. \tag{20.7b}$$

Furthermore $\partial^2/\partial\tau^2 = \partial^2/\partial t^2$. Hence the differential equation for the retarded potential becomes

$$-\frac{1}{4\pi}\,\mathrm{div}\left[\frac{1}{R}\nabla\Psi - \left(\nabla\frac{1}{R}\right)\Psi + \frac{2\mathbf{R}}{R^2}\nabla\frac{1}{c}\frac{\partial\Psi}{\partial t}\right] = \frac{f(\mathbf{r}, t - R/c)}{R}. \tag{20.8}$$

Once more we change the equation in replacing $\mathbf{r}$ by $\mathbf{r}'$ and $\mathbf{r}_0$ of (20.6*a*) by $\mathbf{r}$, using $\mathbf{r}'$ for the source point and $\mathbf{r}$ for field point,

$$-\frac{1}{4\pi}\,\mathrm{div}'\left[\frac{1}{R}\nabla'\Psi - \left(\nabla'\frac{1}{R}\right)\Psi + \frac{2\mathbf{R}}{R^2}\nabla'\frac{1}{c}\frac{\partial\Psi}{\partial t}\right] = \frac{f(\mathbf{r}', t - R/c)}{R} \tag{20.8a}$$

with $\mathbf{R} = \mathbf{r}' - \mathbf{r}$.

We now multiply the equation by the volume element $d\tau'$ and integrate over a region in space between an infinitesimal sphere around the field point $\mathbf{r}$ and an outer closed surface of surface elements

$$d\mathbf{S} = \mathbf{n}\,dS \tag{20.8b}$$

with $\mathbf{n}$ the inside surface normal. The left-hand side can be turned into two surface integrals. The one over the small sphere is easily seen to give the function $\Psi(\mathbf{r}, t)$ itself. Moving the second surface integral to the right-hand

side, on accounting for the change of sign, we find the result

$$\Psi(\mathbf{r}, t) = \int \frac{f(\mathbf{r}', t - R/c)}{R}\, d\tau' + \frac{1}{4\pi}\int\left[-\frac{1}{R}\frac{\partial\Psi}{\partial n} + \left(\Psi + \frac{2R}{c}\frac{\partial\Psi}{\partial t}\right)\frac{\partial}{\partial n}\left(\frac{1}{R}\right)\right] dS, \quad (20.9)$$

with $\partial/\partial n = \mathbf{n}\nabla$, $\mathbf{n}$ the inside normal.

On moving the outer boundary of the region to infinity the formula becomes equivalent with (20.4). For finite regions it requires the knowledge of Ψ, $\partial\Psi/\partial n$, and $\partial\Psi/\partial t$ on the boundary surface.

Spectral Distribution of the Wave Function

Consider the Fourier representation of a field source

$$f(\mathbf{r}, t) = \int_{-\infty}^{\infty} \varphi(\mathbf{r}, \omega) \exp(i\omega t)\, d\omega \quad (20.10)$$

and the corresponding wave function

$$\Psi(\mathbf{r}, t) = \int_{-\infty}^{\infty} \mathcal{U}(\mathbf{r}, \omega) \exp(i\omega t)\, d\omega. \quad (20.10a)$$

The functions $\varphi(\mathbf{r}, \omega)$ and $\mathcal{U}(\mathbf{r}, \omega)$ may conveniently be called spectral functions or Fourier transforms. From (20.5) they are easily seen to be connected by the differential equation

$$(\nabla^2 + k^2)\mathcal{U} = -4\pi\varphi, \qquad k = \omega/c. \quad (20.11)$$

The condition that f and Ψ be real functions requires $f(\mathbf{r}, -\omega) = f(\mathbf{r}, \omega)$ and correspondingly for $\mathcal{U}$.

In principle the three-dimensional spatial wave equation (20.11) can be solved in a somewhat simpler way than the four-dimensional space-time wave equation. The solution can be obtained by means of a Green's function which is defined as a special solution of the homogeneous equation (20.11). To be accurate we write

$$(\nabla^2 + k^2)G(\mathbf{r}) = -4\pi\delta(\mathbf{r}), \quad (20.12)$$

where $\delta(\mathbf{r})$ is a three-dimensional Dirac delta function whose value is zero everywhere except just in the singular point $\mathbf{r} = 0$ in which it becomes infinitely large.

To express the fundamental properties of this function we may think of it as replaced by a function that has a very large value in $\mathbf{r} = 0$ and rapidly decreases to zero in the immediate neighborhood, however, so that the space

integral is finite and has the definite value

$$\int \delta(\mathbf{r})\, d\tau = 1. \tag{20.12a}$$

This only expresses the additional conditions to be imposed on $G(\mathbf{r})$, namely,

$$\int G(\mathbf{r})\, d\tau = 0, \qquad -\frac{1}{4\pi}\int \operatorname{div} \nabla G(\mathbf{r})\, d\tau = 1, \tag{20.13}$$

if the integrals are taken over an infinitesimal region around $\mathbf{r} = 0$. It is found that

$$G(\mathbf{r}) = \frac{\exp(-ikr)}{r}, \tag{20.14}$$

is a solution of (20.12) which satisfies the above condition. Another solution with a positive exponent is also possible, but the former is preferred because it leads to retarded rather than advanced potentials.

From the above definitions it follows that

$$\mathcal{U}(\mathbf{r}, \omega) = \int G(\mathbf{r} - \mathbf{r}')\Phi(\mathbf{r}', \omega)\, d\tau' \tag{20.15}$$

with extension of the integral over the entire space. Writing for abbreviation

$$\mathbf{R} = \mathbf{r} - \mathbf{r}', \qquad G(\mathbf{r} - \mathbf{r}') = \frac{\exp(-i\omega R/c)}{R}, \tag{20.15a}$$

we multiply (20.15) by $\exp(i\omega t)\, d\omega$ and integrate in the frequency variable. The result is easily seen to be

$$\Psi(\mathbf{r}, t) = \int \frac{f(\mathbf{r}', t - R/c)}{R}\, d\tau' \tag{20.16}$$

in conformity with (20.9) for an infinitely remote boundary.

To obtain the full formula (20.9) for a bounded region we have to combine (20.11) and (20.12) replacing the variable $\mathbf{r}$ by $\mathbf{r}'$, however, with the argument $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ in $G(\mathbf{r})$. From the equation we obtain by combination

$$-\frac{1}{4\pi}\operatorname{div}' [G(\mathbf{R})\nabla'\mathcal{U}(\mathbf{r}, \omega) - \mathcal{U}(\mathbf{r}', \omega)\nabla' G(\mathbf{R})] = G(\mathbf{R})\varphi(\mathbf{r}', \omega) - \mathcal{U}(\mathbf{r}', \omega)\, \delta(\mathbf{R}). \tag{20.17}$$

Space integration on the right-hand side gives (20.15). However, if the integral is over a finite region, the left-hand side is different from zero. When transformed into a surface integral this is only to be taken on the outer boundary, since the discontinuity of $G(\mathbf{R})$ in $\mathbf{R} = 0$ has already been taken care of by the right-hand side delta function $\delta(\mathbf{R})$.

Transferring the surface integral to the right-hand side and referring to the inside normal $\mathbf{n}$ and surface element $d\mathbf{S} = \mathbf{n}\, dS$, we find that the additional surface becomes

$$\frac{1}{4\pi}\int\left[-G(\mathbf{R})\frac{\partial}{\partial n}\mathcal{U}(\mathbf{r}', \omega) - \mathcal{U}(\mathbf{r}', \omega)\frac{\partial}{\partial n}G(\mathbf{R})\right] dS$$

$$= \frac{1}{4\pi}\int\left\{-\frac{1}{R}\frac{\partial}{\partial n}[\mathcal{U}(\mathbf{r}', \omega)\exp(-ikR)]\right.$$

$$\left. + \mathcal{U}(\mathbf{r}', \omega)\exp(-ikR)(1 + 2ikR)\frac{\partial}{\partial n}\left(\frac{1}{R}\right)\right\} dS. \quad (20.18)$$

We first observe that $k = \omega/c$ and that according to (20.10*a*) multiplication of the spectral function (Fourier transform) with $i\omega$ corresponds to the time derivative of the space-time functions. Next by multiplying (20.18) by $\exp(i\omega t)$ and integrating over the frequency space, the result is easily seen to be the additional surface integral in (20.9).

The aim of the Green's method is of course not simply to demonstrate the correctness of the most compact field source representation of the wave function as given in (20.9). In fact, for that purpose it is more cumbersome than the direct method. Its usefulness rests on its application to special problems in order to avoid intricate integration processes or at least to postpone this part of the process to the latest possible stage. In reality, therefore, Green's method is only an expedient for the evaluation of the definite integrals.

Green's Function in Four Dimensions

The solution of the wave equation (20.5) can also be written

$$\Psi(\mathbf{r}, t) = \int G(\mathbf{r} - \mathbf{r}', t - t')f(\mathbf{r}', t')\, d\tau'\, d\tau' \quad (20.19)$$

by means of a Green's function obeying the differential equation

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)G(\mathbf{r}, t) = -4\pi\,\delta(\mathbf{r})\,\delta(t). \quad (20.20)$$

For the purpose of widest possible freedom in the integration process the product delta function is written

$$\delta(\mathbf{r})\,\delta(t) = \frac{1}{(2\pi)^4}\int \exp[i(\omega t - \mathbf{kr})]\, d^3\mathbf{k}\, d\omega. \quad (20.21)$$

For those not familiar with the delta function an explanation is needed. Consider

$$\delta(t, \Omega) = \frac{1}{2\pi}\int_{-\Omega}^{\Omega}\exp(i\omega t)\, d\omega = \frac{1}{\pi t}\sin(\Omega t) \quad (20.21a)$$

and

$$\int_{-\varepsilon}^{\varepsilon} \delta(t, \Omega)\, dt = \frac{1}{\pi} \int_{-\varepsilon}^{\varepsilon} \frac{\sin \Omega t}{t}\, dt = \frac{1}{\pi} \int_{-\varepsilon\Omega}^{\varepsilon\Omega} \frac{\sin x}{x}\, dx. \tag{20.21b}$$

However small ε is, the limits of integration tend to $\pm\infty$ as $\Omega \to \infty$. The left-hand integral is known to be equal to π for the above limits. Hence the result is

$$\lim_{\Omega\to\infty} \int_{-\varepsilon}^{\varepsilon} \delta(t, \Omega)\, dt = 1; \tag{20.22}$$

this is the meaning of writing

$$\int_{-\varepsilon}^{\varepsilon} \delta(t)\, dt = 1 \tag{20.22a}$$

or even

$$\int \delta(t)\, dt = 1 \tag{20.22b}$$

for nonspecified limits on either side of $t = 0$. It may be supplemented by

$$\int \delta(t)\, dt = 0 \tag{20.22c}$$

for any region outside of $t = 0$.

A still franker mode of description, opposed by mathematicians, is to write

$$\delta(t) = \lim_{\Omega\to\infty} \delta(t, \Omega) \tag{20.22d}$$

for the improper function $\delta(t)$. When taken with a grain of salt, the meaning of the equation might, however, be clear enough with the background of the above considerations.

Expressing the Green's function by an integral similar to (20.21), we easily find from (20.20) that

$$G(\mathbf{r}, t) = \frac{2}{(2\pi)^3} \int \frac{\exp\left(i(\omega t - \mathbf{kr})\right)}{k^2 - \omega^2/c^2}\, d^3\mathbf{k}\, d\omega. \tag{20.23}$$

Owing to the singularities $\omega = \pm ck$ of the integrand, the path of integration in ω needs a closer examination. It is customary to replace the path along the real axis by another path slightly beneath or slightly above the real axis. This is accomplished by replacing ω in the denominator by $\omega - i\varepsilon$ and thus transferring the singular points to $\omega = \pm ck + i\varepsilon$. The two different Green's functions thus obtained for slightly positive and slightly negative ε-value may be denoted by $G_{\pm}$.

We shall consider only the positive ε-value corresponding to a path of integration below the real axis in the complex ω-plane. For negative t-values the path of integration may then be closed by a semicircle in the lower half-plane to give zero value for G. For positive t-values the path may be closed similarly in the upper half-plane and contracted into small circles around the two singular points to allow for evaluation of the frequency integral by the Cauchy theorem. The result is easily found to be

$$G(\mathbf{r}, t) = \frac{2c}{(2\pi)^2} \int \frac{1}{k} \exp(-i\mathbf{kr}) \sin(ckt)\, d^3\mathbf{k}. \tag{20.24}$$

The further integration is performed by using spherical polar coordinates in the **k**-space and gives

$$G(\mathbf{r}, t) = \frac{2c}{\pi r} \int_0^\infty \sin(kr) \sin(ckt)\, dk$$

$$= \frac{c}{\pi r} \int_{-\infty}^{\infty} \sin(kr) \sin(ckt)\, dk, \tag{20.24a}$$

or with $ck = K$

$$G(\mathbf{r}, t) = \frac{1}{2\pi r} \int_{-\infty}^{\infty} \left\{ \cos\left[K\left(t - \frac{r}{c}\right)\right] - \cos\left[K\left(t + \frac{r}{c}\right)\right] \right\} dK$$

$$= \frac{\delta(t - r/c) - \delta(t + r/c)}{r}. \tag{20.24b}$$

The last delta function is zero for positive t and may be removed.

Equation 20.19 now becomes with $\mathbf{R} = \mathbf{r} - \mathbf{r}'$,

$$\Psi(\mathbf{r}, t) = \int \frac{f(\mathbf{r}', t')\, \delta(t - t' - R/c)}{R}\, d\tau'\, dt'$$

$$= \int \frac{f(\mathbf{r}', t - R/c)}{R}\, d\tau'. \tag{20.25}$$

Again the above identification of results from using various forms of Green's functions is only of secondary importance. The main purpose of the four-dimensional Green's function, as well as of other forms of Green's functions, is to allow for integration processes in the most convenient order of the auxiliary variables when the method is applied to some actual problem.

21. MULTIPLE RADIATION

Electric Multipoles in a Vacuum

Consider for simplicity dipole radiation in a vacuum with the dipole $\mathbf{p}(t)$ directed along the z-axis. We repeat the Hertz solution of the homogeneous

electromagnetic equation which may now be written with only two field variables **E** and **H**,

$$\begin{aligned} &\operatorname{div}\mathbf{E}=0, \qquad \operatorname{div}\mathbf{H}=0,\\ &\operatorname{curl}\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t}, \qquad \operatorname{curl}\mathbf{H}=\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}. \end{aligned} \tag{21.1}$$

The solution is from (18.11), (18.12), (19.2), and (19.7):

$$\begin{aligned} &\mathbf{H}=\frac{1}{c}\frac{\partial}{\partial t}\operatorname{curl}\mathbf{Z}, \qquad \mathbf{E}=\operatorname{curl}\operatorname{curl}\mathbf{Z},\\ &\mathbf{Z}=\frac{\mathbf{p}(t-r/c)}{r}. \end{aligned} \tag{21.2}$$

The wave equation

$$\left(\nabla^2-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{Z}=0 \tag{21.3}$$

is satisfied not only by the above **Z** but also by all its derivatives with respect to any of its space variables x, y, z. At this state we shall call attention only to the z-derivatives. If they are used for alternative Hertz vectors, the resulting fields are electric multipole fields. The operator $\partial/\partial z$ commutes with $\partial/\partial t$ and with any of the space differential operators. Hence the nth order fields may be written, for instance,

$$\mathbf{H}_n=(-1)^n\frac{\partial^n}{\partial z^n}\mathbf{H}, \qquad \mathbf{E}_n=(-1)^n\frac{\partial^n}{\partial z^n}\mathbf{E}. \tag{21.4}$$

By (19.9) and (19.11), and with $\mathbf{p}=\mathbf{p}(t-r/c)$, the dipole field vectors are

$$\mathbf{H}=\left(\frac{\dot{\mathbf{p}}}{cr^2}+\frac{\ddot{\mathbf{p}}}{c^2r}\right)\times\frac{\mathbf{r}}{r}, \tag{21.4a}$$

$$\mathbf{E}=\frac{3(\mathbf{rp})\mathbf{r}}{r^5}-\frac{\mathbf{p}}{r^3}+\frac{3(\mathbf{r}\dot{\mathbf{p}})\mathbf{r}}{cr^4}-\frac{\dot{\mathbf{p}}}{cr^2}+\frac{(\ddot{\mathbf{p}}\times\mathbf{r})\times\mathbf{r}}{c^2r^3}. \tag{21.4b}$$

From these equations the multipole fields are obtainable.

By the derivation of r in the argument $t-r/c$ in **p** it is seen that higher derivatives of **p** constantly appear. The wave region therefore divides into an increasing number of zones that may be taken to be the former static and radiation zones, together with an ever-increasing number of intermediate zones.

The zone of highest physical interest is as before the radiation zone. Next comes the static zone which provides for an understanding of the field source.

To obtain the field in the static zone we may be satisfied by studying the scalar potential

$$\Phi = -\text{div } \mathbf{Z} \tag{21.5}$$

and its derivatives with respect to z with the understanding that derivations through $\mathbf{p}(t - r/c)$ can be removed. We therefore have in the static zone, putting $\mathbf{p} = p\mathbf{k}$, on using the operator $(1/n!)(-\partial/\partial z)^{n+1}$

$$\Phi = \frac{pz}{r^3} = P_1(\cos\vartheta)\frac{p}{r^2}, \tag{21.6}$$

and next in succession,

$$\Phi_1 = \frac{1}{2}\frac{p}{r^5}(3z^2 - r^2) = P_2(\cos\vartheta)\frac{p}{r^3}, \tag{21.6a}$$

$$\Phi_2 = \frac{1}{6}\frac{p}{r^7}(15z^3 - 9zr^2) = P_3(\cos\vartheta)\frac{p}{r^4}, \tag{21.6b}$$

$$\Phi_{n-1} = P_n(\cos\vartheta)\frac{p}{r^{n+1}}. \tag{21.6c}$$

Hence it is seen that the sources of the field are multipoles of strength $p(t)$.

For studies of the field in the radiation zone we need retain only those terms resulting from differentiations through $\mathbf{p} = \mathbf{p}(t - r/c)$. Now

$$-\frac{\partial \mathbf{p}}{\partial z} = \frac{\cos\vartheta}{c}\dot{\mathbf{p}}\left(t - \frac{r}{c}\right). \tag{21.7}$$

Hence in the radiation zone

$$\mathbf{Z}_{n-1} = \frac{1}{n!}\frac{1}{r}\left(\frac{\cos\vartheta}{c}\right)^{n-1}\mathbf{p}^{(n-1)}\left(t - \frac{r}{c}\right). \tag{21.8}$$

The field variables are

$$\begin{aligned}\mathbf{H}_{n-1} &= \frac{1}{n!}\left(\frac{\cos\vartheta}{c}\right)^{n-1}\frac{1}{c^2 r}\mathbf{p}^{(n+1)} \times \frac{\mathbf{r}}{r} \\ \mathbf{E}_{n-1} &= \mathbf{H}_{n-1} \times \frac{\mathbf{r}}{r}.\end{aligned} \tag{21.9}$$

Radiation from an Oscillating Magnetic Dipole

As already mentioned, new forms of the Hertz vector can be obtained from the basic solution of the homogeneous equation $\mathbf{Z} = \mathbf{p}(t - r/c)/r$ by application of any of the space-differential operators. If $\mathbf{p}$, and hence $\mathbf{Z}$, are taken in the z-direction, the application of $\partial/\partial x$ and $\partial/\partial y$ would lead to spherical

waves whose radiative source would be hard to identify. Moreover, without allowing for x- and y-directions of the basic vector $\mathbf{Z}$ we cannot by any application of differential operators obtain the most general radiation field in the form of spherical waves.

We therefore note that there are also vectorial differential operators commuting with the operators of the wave equation as, for instance, the curl. We therefore try the new Hertz vector

$$\mathbf{Z}_1 = \operatorname{curl} \mathbf{Z}, \qquad \mathbf{Z} = \frac{\mathbf{p}(t - r/c)}{r}. \tag{21.10}$$

This vector has the advantage that the scalar potential $\Phi_1 = -\operatorname{div} \mathbf{Z}_1$ disappears, so that

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}_1}{\partial t}, \qquad \mathbf{A}_1 = \frac{1}{c}\frac{\partial \mathbf{Z}_1}{\partial t}. \tag{21.11}$$

The vector

$$\mathbf{H} = \operatorname{curl} \mathbf{A}_1 = \frac{1}{c}\frac{\partial}{\partial t} \operatorname{curl} \operatorname{curl} \mathbf{Z} \tag{21.12}$$

now becomes of primary interest. It is seen to be the time derivative of the former $\mathbf{E} = \operatorname{curl} \operatorname{curl} \mathbf{Z}$ as explicitly given in (21.4*b*). In the nearest zone, which is now the induction or magnetostatic zone, the vector becomes

$$\mathbf{H} = \frac{3(\mathbf{r}\dot{\mathbf{p}})\mathbf{r}}{cr^5} - \frac{\dot{\mathbf{p}}}{cr^3} = -\nabla \frac{\mathbf{r}\dot{\mathbf{p}}}{cr^3}. \tag{21.13}$$

Hence it corresponds to a radiation source consisting of a time-dependent magnetic dipole $\dot{\mathbf{p}}(t)/c$ with a magnetic potential

$$\Phi_m = \frac{1}{c}\frac{\mathbf{r}\dot{\mathbf{p}}}{r^3}. \tag{21.13a}$$

Because of

$$\mathbf{Z}_1 = \left(\frac{\mathbf{p}}{r^3} + \frac{\dot{\mathbf{p}}}{cr^2}\right) \times \mathbf{r} \tag{21.13b}$$

the field variables in the radiation zone become

$$\mathbf{E} = -\frac{\ddot{\mathbf{p}} \times \mathbf{r}^0}{c^3 r}, \qquad \mathbf{H} = \frac{(\ddot{\mathbf{p}} \times \mathbf{r}^0) \times \mathbf{r}^0}{c^3 r} = \mathbf{r}^0 \times \mathbf{E} \tag{21.14}$$

With respect to field strength the radiation field of the magnetic dipole corresponds to the electric quadrupole, and the wave normal and the field vectors $\mathbf{r}^0$, $\mathbf{E}$, an $\mathbf{H}$ still form a right-hand orthogonal system.

However, the roles of the vectors **E** and **H** with respect to direction have been interchanged, so that **H** is now in the (**p**, **r**) plane and **E** is along a circle of latitude on the wave surface sphere of radius r.

Radiation from an Oscillating Charge and a Linear Antenna

A solution of the homogeneous wave equation for a Hertz vector corresponding to an oscillating charge

$$\mathbf{p}(t) = e\mathbf{q}(t) \tag{21.15}$$

has proved extremely difficult to find. One might be tempted to try as an approximate solution

$$\mathbf{Z} = \frac{\mathbf{k}eq(t - r'/c)}{r'} \tag{21.16}$$

with

$$r' = (r^2 - 2zq + q^2)^{1/2} \simeq r - \cos\vartheta q(t). \tag{21.16a}$$

In the radiation zone this gives

$$\begin{aligned}\mathbf{Z} &= \frac{\mathbf{k}e}{r} q\left[t - \frac{r}{c} + \cos\vartheta \frac{q(t)}{c}\right] \\ &= \frac{\mathbf{k}e}{r}\left[q\left(t - \frac{r}{c}\right) + \frac{\cos\vartheta}{c} q(t)\dot{q}\left(t - \frac{r}{c}\right) + \cdots\right],\end{aligned} \tag{21.16b}$$

but this is an expansion with quite different terms from those of (21.8) and (21.9). Because of the extra powers of $q(t)$ the higher terms even involve radiation with frequencies of 2ω, 3ω, $\cdots$.

To have an expansion in the form of monochromatic oscillating multipole terms we have to consider a true physical dipole oscillating with the single frequency ω. This can be realized by means of two small conducting spheres connected by a straight conducting wire in which flows an alternating current, as in Fig. 3-3. This, however, belongs to the theory of antennas which for the sake of brevity we shall not discuss further.

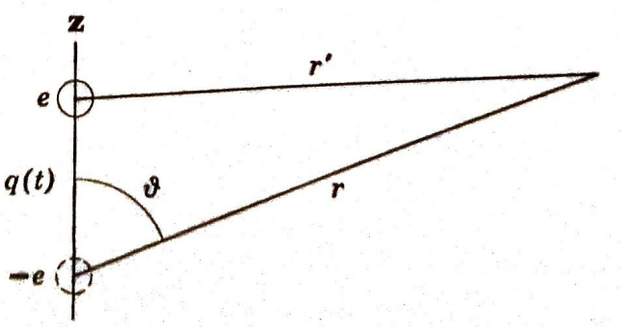

Fig. 3-3. Oscillating charge.

22. FIELDS OF MOVING PARTICLES

Generalization of the Coulomb Law

Consider the homogeneous wave equations for the electromagnetic potentials, together with the Lorentz convention

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)(\Phi, \mathbf{A}) = 0, \qquad \operatorname{div}\mathbf{A} + \frac{1}{c}\frac{\partial \Phi}{\partial t} = 0. \tag{22.1}$$

The equations are easily seen to be satisfied by the space- and time-dependent functions

$$\Phi = \frac{e}{s}, \qquad \mathbf{A} = \boldsymbol{\beta}\frac{e}{s}, \qquad \boldsymbol{\beta} = \frac{\mathbf{v}}{c}, \tag{22.2}$$

where $\boldsymbol{\beta}$ is a constant vector and

$$s^2 = (x^2 + y^2)(1 - \beta^2) + (z - vt)^2. \tag{22.3}$$

The potentials can be ascribed to an electric point charge e moving with the velocity $\mathbf{v}$ in the direction of the z-axis and which passes the origin at the retarded time

$$t' = t - \frac{r}{c}, \qquad r = (x^2 + y^2 + z^2)^{1/2}. \tag{22.4}$$

Also introducing the coordinates

$$Z = z - vt \qquad \text{and} \qquad \zeta = \gamma Z, \qquad \gamma = \frac{1}{(1 - \beta^2)^{1/2}}, \tag{22.5}$$

we may find it convenient to define the distances R and S by the equations

$$R = (x^2 + y^2 + Z^2)^{1/2}, \qquad S = (x^2 + y^2 + \zeta^2)^{1/2} = \gamma s, \tag{22.6}$$

together with the corresponding vectors $\mathbf{r}$, $\mathbf{R}$, $\mathbf{s}$, and $\mathbf{S}$, all of them pointing toward the field point. The quantities are visualized in Fig. 3-4.

As seen in the figure there are two distances s, the one defined by (22.3) as the distance from the field point to a point p somewhat displaced to the side of the charge e. The other equally great distance is

$$s = r - \boldsymbol{\beta}\mathbf{r}. \tag{22.7}$$

If at time $t = 0$ the charge is at the origin Q, the source point, the traveling time for the electromagnetic action to P, is r/c. In this time the electron has traveled the distance βr, and s corresponds to the definition (22.7). From (22.3) we find

$$s^2 = r^2 - 2z\beta r + \beta^2(r^2 - x^2 - y^2) = (r - \beta z)^2, \tag{22.8}$$

and by $\beta z = \boldsymbol{\beta}\mathbf{r}$ this proves the identity of (22.3) and (22.7).

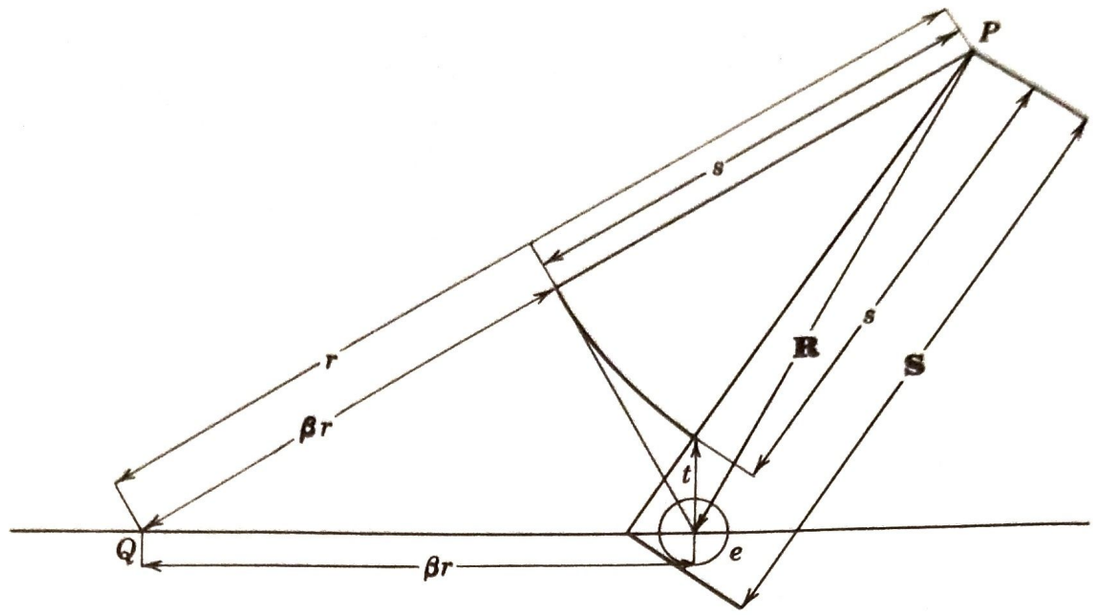

Fig. 3-4. The field from a moving charge.

From (22.2) and (22.3) the electric and magnetic field vectors are found to be

$$\mathbf{E} = \frac{e\mathbf{R}(1-\beta^2)}{s^3}, \qquad \mathbf{H} = \boldsymbol{\beta} \times \mathbf{E}. \tag{22.9}$$

Since $r\boldsymbol{\beta} = \mathbf{r} - \mathbf{R}$ we may also write

$$\mathbf{H} = \mathbf{n} \times \mathbf{E} \tag{22.9a}$$

with $\mathbf{n} = \mathbf{r}^0 = \mathbf{r}/r$ the unit vector in the direction Q to P.

As is easily seen the field follows the motion of the particle. The electric vector is a central force emerging from the simultaneous position point of the particle. Its magnitude, however, depends on the polar angle of the direction through the modified distance s.

Energy and Momentum of an Evenly Moving Particle

Replacing s by S/γ, we find that the density of electric and magnetic field energy becomes

$$u_e = \frac{e^2}{8\pi}\frac{\gamma^2\mathbf{R}^2}{S^6}, \qquad u_m = \frac{e^2}{8\pi}\frac{\gamma^2(x^2+y^2)}{S^6}\beta^2. \tag{22.10}$$

Multiplying by

$$dx\,dy\,dz = \frac{1}{\gamma}dx\,dy\,d\zeta = \frac{1}{\gamma}S^2\,dS\sin\vartheta\,d\vartheta\,d\varphi \tag{22.10a}$$

and integrating in the equatorial angle φ, we find

$$U = U_e + U_m = \frac{\gamma e^2}{4}\int \frac{\sin^2\vartheta(1+\beta^2) + (1-\beta^2)\cos^2\vartheta}{S^2}\,dS\sin\vartheta\,d\vartheta. \tag{22.10b}$$

Assuming the surface of the particle to be given by the surface $S = S_0$ with its charge on the surface and with no inside field, we obtain the total field energy

$$U = \frac{\gamma e^2}{2S_0}\left(\frac{1+\beta^2}{3}\right). \tag{22.11}$$

The surface $S = S_0$ or

$$S^2 = x^2 + y^2 + \frac{(z-vt)^2}{1-\beta^2} = S_0^2 \tag{22.12}$$

is an ellipsoid with a semiaxis S_0 in the transverse direction and $S_0\sqrt{1-\beta^2}$ in direction of the motion. It may be thought of as a sphere of radius S_0 contracted according to the Fitzgerald-Lorentz hypothesis.

According to (16.8) the momentum density of the field is given by $\mathbf{g} = (1/4\pi c)\mathbf{E} \times \mathbf{H}$. From (22.9) we find

$$\mathbf{g} = \frac{1}{4\pi c}(\boldsymbol{\beta}\mathbf{E}^2 - \mathbf{E}(\boldsymbol{\beta}\mathbf{E})) = \frac{\boldsymbol{\beta}}{4\pi c}(E_x^2 + E_y^2) + \frac{1}{4\pi c}(\boldsymbol{\beta}E_z^2 - \mathbf{E}\beta E_z) \tag{22.13}$$

as divided into a parallel and a transverse component. On integrating over the same space as in (22.10*a*) and (22.10*b*) the result is

$$\mathbf{G} = \int \mathbf{g}\, d\tau = \boldsymbol{\beta}\frac{\gamma e^2}{2S_0 c}\frac{4}{3} = \frac{\mathbf{v}U}{c^2}\frac{4}{3+\beta^2}. \tag{22.13a}$$

Hence for high velocities, $v \to c$, the charge behaves like a relativistic particle with respect to the correlation of energy and momentum.

The Liénard-Wiechert Potentials

The potentials (22.2) are known as the Liénard-Wiechert potentials of a moving point charge. We are now going to prove that they are valid also for accelerated charges. We can no longer use (22.3) as a general definition of s. If, however, we replace it by (22.7) we are no longer dependent on a particular coordinate system. Nevertheless the example provided by Fig. 3-4 is valid apart from the position of the charge at time t which is a different one.

The form in which the potentials are still valid may conveniently be written

$$\Phi = \left(\frac{e}{s}\right)_{\text{ret}}, \qquad \mathbf{A} = \left(\frac{e\boldsymbol{\beta}}{s}\right)_{\text{ret}}, \tag{22.14}$$

with the understanding of the subscript that not only

$$s = r - \boldsymbol{\beta}\mathbf{r} \tag{22.14a}$$

but also $\boldsymbol{\beta}$ in the nominator of the expression for $\mathbf{A}$ be taken at the retarded time $t' = t - r/c$ to replace the time $t' = 0$ as assumed in the figure.

To prove the validity of (22.14) we consider the moving point charge a limiting case of a particular continuous charge and current distribution and make use of the solutions of the corresponding inhomogeneous wave equations. In dealing with point charges, which actually means charged particles, it has proved to be the more convenient method to use directly the potentials

$$\Phi = \int \frac{\rho(\mathbf{r}', t - r/c)}{r} d\tau', \qquad \mathbf{A} = \frac{1}{c} \int \frac{\mathbf{j}(\mathbf{r}', t - r/c)}{r} d\tau', \tag{22.15}$$

rather than the Hertz vector

$$\mathbf{Z} = \int \frac{\mathbf{p}(\mathbf{r}', t - r/c)}{r} d\tau'. \tag{22.15a}$$

Even though the expressions (22.15) are well established from the corresponding inhomogeneous equations, their direct deductions from $\mathbf{Z}$ are of principal interest. From

$$\Phi = -\operatorname{div} \mathbf{Z}, \qquad \mathbf{A} = \frac{1}{c} \frac{\partial \mathbf{Z}}{\partial t} \tag{22.15b}$$

and

$$\rho = -\operatorname{div} \mathbf{p}, \qquad \mathbf{j} = \frac{\partial \mathbf{p}}{\partial t} \tag{22.15c}$$

it is seen that the expression for $\mathbf{A}$ is obtained directly from $\mathbf{Z}$. To arrive at the expression for Φ, however, we have to note that

$$\operatorname{div} \frac{\mathbf{p}}{r} = -\operatorname{div}' \frac{\mathbf{p}}{r} - \frac{\rho(\mathbf{r}', t - r/c)}{r} \tag{22.15d}$$

with the prime referring to the coordinates of the source point Q. This is to be understood, so that on applying the operator div′ to $\mathbf{p}/r$, we are not following the route of the operator div to the distance r from Q to the field point P. The div′ applies also to the arguments $\mathbf{r}'$ in $\mathbf{p}$ for which must be corrected by the last term of (22.15*d*) according to the first equation of (22.15*c*). By the Gauss theorem the integral over the first right-hand term of (22.15*d*) as extended over the entire space vanishes, and hence also the expression (22.15) for Φ.

To avoid confusion let us write

$$\mathbf{r} = \mathbf{R} - \mathbf{R}' \tag{22.16}$$

with arbitrary origin for the field and source point coordinates $\mathbf{R}$ and $\mathbf{R}'$. Then we also have

$$\Phi = \int \frac{\rho(\mathbf{R}', t')}{|\mathbf{R} - \mathbf{R}'|} \delta\left(t - \frac{|\mathbf{R} - \mathbf{R}'|}{c} - t'\right) d\tau' \, dt'. \tag{22.17}$$

Again for a point charge we write

$$\rho(\mathbf{R}, t) = e\,\delta(\mathbf{R} - R'(t)). \tag{22.17a}$$

On performing space integration we obtain

$$\Phi = \int \frac{e}{|\mathbf{R} - R'(t')|}\,\delta\left(t - \frac{|\mathbf{R} - R'(t')|}{c} - t'\right) dt' \tag{22.18}$$

and for this again with some reservation we write

$$\Phi(\mathbf{r}, t) = \int \frac{e}{r(t')}\,\delta\left(t - \frac{r(t')}{c} - t'\right) dt'. \tag{22.18a}$$

According to the peculiarity of the delta function we can write

$$\delta\left(t - \frac{r(t')}{c} - t'\right) = \delta(t - (1 - \beta_r)t') \tag{22.18b}$$

with

$$\beta_r = -\frac{1}{c}\frac{d}{dt'}\,r(t') = \frac{1}{c}\frac{\mathbf{r}}{r}\,\dot{\mathbf{R}}(t') = \frac{1}{c}\,v_r(t') \tag{22.18c}$$

with $\mathbf{v}(t') = \dot{\mathbf{R}}(t')$ the velocity of the point charge. On changing the variable t' and performing the integration the result is

$$\Phi = \frac{e}{r(1 - \beta_r)} = \frac{e}{r - \boldsymbol{\beta}\mathbf{r}} = \frac{e}{s} \tag{22.19}$$

with $r = |\mathbf{R} - \mathbf{R}'(t')|$ taken at the retarded time $t' = t - r/c$. The construction of the potential corresponds entirely to the view that a sphere around the field point contracting with the velocity of light takes a different time to sweep over a moving charge than over a charge at rest, namely, in the proportion of $c/(c - v_r)$.

Field Vectors of Accelerated Charges

To evaluate the field vectors for an accelerated charge, we may proceed differently and it is hard to tell what is the simplest way. We might follow the patterns of (22.15*a*) to (22.15*d*) which led from the Hertz vector to the potentials, and proceed similarly to have the field vectors expressed by space integrals. Even though some details are easily obtained in this way, the method implies partial integrations which require even more care than the use of the standard method of basing the calculations directly on the Liénard-Wiechert potentials.

The procedure may be abbreviated by dropping in the calculations those terms already known which depend only on $\mathbf{v}$ and retain only those depending on the acceleration $\dot{\mathbf{v}}$. The operators used for the purpose will be denoted ∇_a and $(\partial/\partial t)_a$.

The point is that by differentiation of potentials for accelerated charges we must consider the retarded time t' a function of the space and time variables according to the equation

$$t = t' + \frac{r(t')}{c} \tag{22.20}$$

which, as we have seen, leads to the derivative

$$\frac{\partial t'}{\partial t} = \frac{1}{1 - \beta_r} = \frac{r}{s}. \tag{22.21}$$

Next it also yields

$$\nabla t' = -\frac{\mathbf{r}}{cr}\frac{1}{1 - \beta_r} = -\frac{\mathbf{r}}{cs}. \tag{22.21a}$$

From these auxiliary equations we fairly easily arrive at the equations

$$\nabla_a s = -(\dot{\boldsymbol{\beta}}\mathbf{r})\,\nabla t' = \frac{1}{cs}(\dot{\boldsymbol{\beta}}\mathbf{r})\mathbf{r}, \tag{22.22}$$

$$\frac{1}{c}\left(\frac{\partial s}{\partial t}\right)_a = -\frac{1}{c}(\dot{\boldsymbol{\beta}}\mathbf{r})\frac{\partial t'}{\partial t} = -\frac{1}{cs}(\dot{\boldsymbol{\beta}}\mathbf{r})r, \tag{22.22a}$$

$$\operatorname{curl}\boldsymbol{\beta} = \nabla t' \times \dot{\boldsymbol{\beta}} = \frac{1}{cs}(\dot{\boldsymbol{\beta}} \times \mathbf{r}). \tag{22.22b}$$

Inserting in the equations

$$\mathbf{E}_a = \frac{e}{s^2}\left(\nabla_a s + \frac{\boldsymbol{\beta}}{c}\frac{\partial s}{\partial t} - \frac{\dot{\boldsymbol{\beta}}}{c}r\right), \tag{22.23}$$

$$\mathbf{H}_a = \frac{e}{s^2}(\boldsymbol{\beta} \times (\nabla_a s) + s \operatorname{curl}\boldsymbol{\beta}), \tag{22.23a}$$

we obtain the result

$$\mathbf{E}_a = \frac{e}{cs^3}[(\mathbf{r} - r\boldsymbol{\beta})(\mathbf{r}\dot{\boldsymbol{\beta}}) - \dot{\boldsymbol{\beta}}sr], \tag{22.24}$$

$$\mathbf{H}_a = \frac{e}{cs^3}[-(\mathbf{r} \times \boldsymbol{\beta})(\mathbf{r}\dot{\boldsymbol{\beta}}) - (\mathbf{r} \times \dot{\boldsymbol{\beta}})s]. \tag{22.24a}$$

Observing that

$$sr = r^2 - r(\mathbf{r}\boldsymbol{\beta}) = \mathbf{r}(\mathbf{r} - r\boldsymbol{\beta}), \tag{22.24b}$$

we finally obtain

$$\mathbf{E}_a = \frac{e}{cs^3}\mathbf{r} \times ((\mathbf{r} - r\boldsymbol{\beta}) \times \dot{\boldsymbol{\beta}}), \tag{22.25}$$

$$\mathbf{H}_a = \frac{\mathbf{r}}{r} \times \mathbf{E}_a. \tag{22.25a}$$

Radiation from an Oscillating Charged Particle

Consider an elastically bound charged particle that oscillates with a certain finite amplitude $\mathbf{q}(t)$ as shown in Fig. 3-5. In the radiation zone we need no longer discriminate between the true field point vector from the charge and the vector from its central position. Thus it might appear that the difference in radiation from a Hertz dipole of the same strength and frequency may be fairly unimportant and contained simply in the term $-r\boldsymbol{\beta}$ in the central factor of (22.25).

The main difference comes, however, from the denominator s^3 of (22.25) which must now be replaced by

$$s = r(1 - \beta_r) = r\left(1 - \frac{\dot{q}(t)}{c}\cos\vartheta\right). \tag{22.26}$$

Introducing the wave normal $\mathbf{n} = \mathbf{r}/r$ in the radiation zone, we find that the electric field vector becomes

$$\mathbf{E}_a = \frac{e}{c^2 r}\frac{\mathbf{n} \times [(\mathbf{n} - (1/c)\dot{\mathbf{q}}) \times \ddot{\mathbf{q}}]}{(1 - \mathbf{n}\dot{\mathbf{q}}/c)^3}, \tag{22.27}$$

where the quantities $\dot{\mathbf{q}}$ and $\ddot{\mathbf{q}}$ should be taken at the retarded time $t' = t - r/c$; but this is not of importance anymore for the calculation of radiated energy, since r is now independent of t.

Expanding the denominator in terms of $\mathbf{n}\dot{\mathbf{q}}$, we obtain a first-order approximation

$$\mathbf{E}_a = \frac{e}{c^2 r}(\mathbf{n} \times (\mathbf{n} \times \ddot{\mathbf{q}})) \tag{22.27a}$$

corresponding to the Hertz dipole, followed by powers of $\mathbf{n}\dot{\mathbf{q}}/c$ of relative strength $\cos\vartheta a\omega/c$ for each ascending power, with a the maximum amplitude. Simultaneously the radiation frequency takes new multiple values 2ω, $3\omega, 4\omega, \cdots$.

This is in conformity with (21.16).

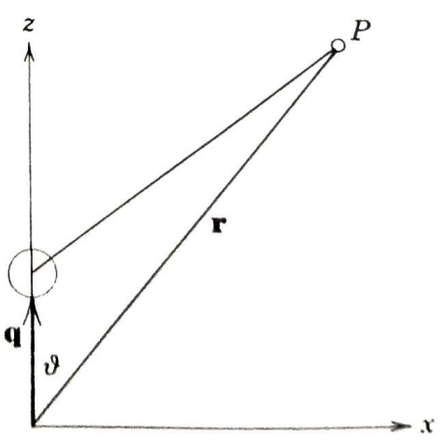

Fig. 3-5. Oscillating charged particle.

The Cherenkov Radiation

Up to now it was tacitly assumed that the velocity of the charged particle was smaller than that of light. According to relativity theory this is always true in empty space, $v < c$. In a dielectric, however, the speed of light is $c' = c/\sqrt{\varepsilon}$, if for simplicity we take $\mu = 1$. In that case we also have to consider the possibility that $v > c'$, and this leads to a special phenomenon called Cherenkov radiation after its discoverer.

The main features of the electromagnetic equations for material substances are retained on simply replacing c' by c. In order to make use of equations that are already at hand we write provisionally c for c' with the effect that we shall also have to consider the case $\beta > 1$. To obtain the Cherenkov radiation it suffices to study the simpler case of a particle moving with the constant velocity $\mathbf{v} = c\boldsymbol{\beta}$.

The Liénard-Wiechert potentials need no other modification than the multiplication of Φ with $1/\sqrt{\varepsilon}$ and a redefinition of the distance s into

$$s = [(z - vt)^2 - (x^2 + y^2)(\beta^2 - 1)]^{1/2}. \tag{22.28}$$

In order that this quantity be real the field point must be inside a cone with the apex in the moving charge and the opening angle ϑ given by

$$\sin \vartheta = \frac{1}{\beta} = \frac{c}{v}. \tag{22.28a}$$

It is obvious also that this must be the rear cone as illustrated in Fig. 3-6.

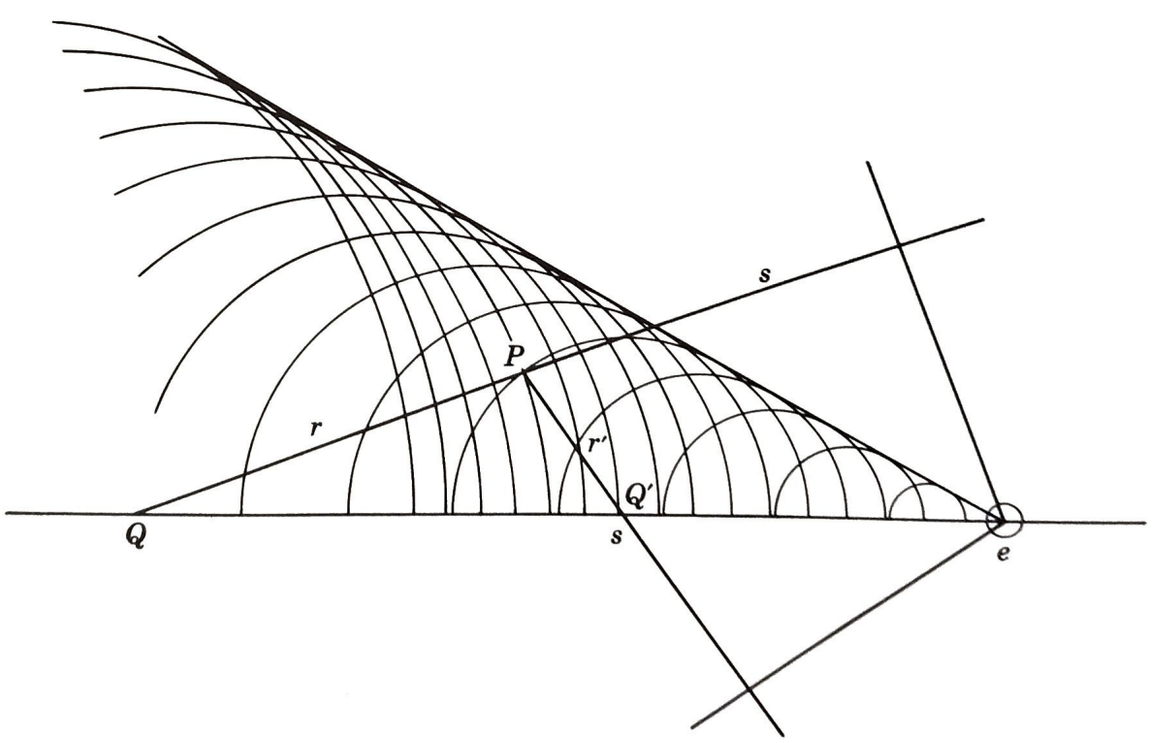

Fig. 3-6. Cherenkov radiation.

It is also seen that any field point P is hit simultaneously by waves from two different source points Q and Q', and this is what makes the essential difference from the ordinary case of an evenly moving charge.

The double value of the length of the "ray" r is found as follows. Replace vt by βr in the expression (22.28) for s. Then from the equation

$$\begin{aligned} s^2 &= (1 - \beta^2)(x^2 + y^2) + (z - \beta r)^2 \\ &= r^2 - 2\beta z r + \beta^2(r^2 - x^2 - y^2) = (r - \beta z)^2, \end{aligned} \tag{22.29}$$

which is essentially the same as (22.7), we obtain the double root

$$r = \beta z - s, \qquad r = \beta z + s. \tag{22.30}$$

The length s is here the distances from P to the projection of the charge on the two rays. The quantity βz is positive and negative, respectively. It is the projection of Qe or $Q'e$ on either ray, with positive and negative sign, respectively.

The two distances s being equal, the Linéard-Wiechert potentials become

$$\Phi = 2\frac{e}{\varepsilon s}, \qquad \mathbf{A} = 2\frac{e\mathbf{v}}{s}. \tag{22.31}$$

The field vectors are easily found:

$$\mathbf{E} = \frac{2e(1 - \beta^2)\mathbf{R}}{\varepsilon s^3}, \qquad \mathbf{H} = \boldsymbol{\beta} \times \varepsilon\mathbf{E}, \tag{22.32}$$

where $\mathbf{R}$ is the vector from the charge e to the field point P.

The Poynting vector is

$$\mathbf{S} = \frac{c}{4\pi}\mathbf{E} \times \mathbf{H} = \frac{4e^2c(1 - \beta^2)^2}{4\pi\varepsilon s^6}\mathbf{R} \times (\boldsymbol{\beta} \times \mathbf{R}). \tag{22.33}$$

It may also be written

$$\mathbf{S} = \frac{4e^2v(\beta^2 - 1)^2}{4\pi\varepsilon s^6}R^2\mathbf{n} \tag{22.33a}$$

where $\mathbf{n}$ is a unit vector playing the role of a normal wave. This is the direction of energy transport which is normal to $\mathbf{R}$. At the surface of the cone it becomes normal to the surface. Here the radiation has the character of a shock wave.

The true origin of the Cherenkov radiation is, of course, the acceleration of electric particles of the dielectric medium. The spectrum of the radiation will be highly polychromatic. A description of the radiation on the basis of a single phenomenological dielectric constant ε or refraction index $n = \sqrt{\varepsilon}$

will therefore be highly inadequate. The process will be widely different in a dispersive medium.

An immediate use of the Cherenkov radiation has been to measure the velocity of high speed electric particles by observing the direction of shock waves produced in media of high dielectric constants and correspondingly slow propagation of electromagnetic waves.

PART IV

Atomic Theory

Introduction

Part IV contains an exposition of the theoretical treatment of atoms. I have not been able to include all the topics that I had hoped to consider. The very interesting subjects of atoms containing several electrons and of the simplest molecules—which have occupied my interest for so many years—unfortunately had to be omitted because of the limited space available. This circumstance is mainly due to the fact that the fundamental problems of perturbation and scattering for electrons and electromagnetic radiation have received a fairly extensive treatment.

In the first chapter of Part IV I have tried to illuminate, in a fairly detailed manner, the general experimental and theoretical basis of quantum theory. In Chapter 2 the atomic theory of Bohr is discussed, both from the elementary and from the more mathematical point of view. The latter part may seem to have received too much attention if this book is to be regarded as a purely introductory text; however, I have felt it desirable that the reader should be able to find answers to the questions that will certainly arise in the course of a closer study of the theory. However, even if the reader should omit this more advanced discussion, he will hardly have any cause for objection to the fact that Bohr's atomic theory has been included in the book, in view of the prominent role that is still played by the associated classical notions in our attempts to understand atomic processes.

The presentation of wave mechanics in Chapters 3 to 5 more or less follows the usual lines. However, topics of a more general character—such as matrix-mechanical methods—are frequently introduced and discussed, particularly in the latter chapters. In Chapter 3 I have attempted, by almost heuristic methods, to establish the most important basic notions: above all the reinterpretation of dynamic variables as operators, with associated eigenvalues, eigenstates, and matrix elements. In Chapter 4 the primary applications of the theory, in particular to the atomic Kepler problem, are considered. In view of the prominent role played by the concept of spin in atomic theory,

I have considered the orbital and intrinsic spins of electrons in rather great detail in this chapter; moreover, matrix-mechanical methods have been extensively employed in order to obtain the most general presentation and also to prepare for the transition to relativistic wave mechanics. Chapter 5 on relativistic quantum theory is comparatively short. The intention here has been to present the mathematical foundations of the theory and to illuminate the chief features of electron spin and the fine structure of atomic states, rather than discuss the multifarious applications.

Finally I have discussed, in a fairly detailed manner, the most important features of perturbation and scattering, in Chapters 6 and 8, respectively.* The first part of the argument is semiclassical and must be supplemented by considerations of correspondence, in order to lead to some insight into the problems of absorption and coherent scattering, and also the more difficult problems of emission and incoherent scattering of electromagnetic radiation. Toward the end of the book I have attempted to supplement the presentation by quantum-electrodynamic considerations, which lead to a deeper understanding of the processes of emission and incoherent scattering and culminate in the complete quantum-theoretic dispersion formula. The scattering of electrons or other atomic particles has been treated both by means of the Born approximation method and by the partial-wave method of Rayleigh. Although these two chapters are rather weighty for an introductory text, I have (as emphasized earlier) not wished to restrict my exposition to serve only this purpose; an adequate discussion of these topics is bound to become rather involved, by any method of presentation.

The execution of that task which I set myself several years ago,—to write a coherent account of the main subjects of modern theoretical physics and atomic physics—has presented more difficulties than I had expected. I am grateful to my previously mentioned coworkers, who have persevered faithfully in their assistance up to the publication of this work. Finally, I would like to express the hope that these volumes will meet a need and be of use to as many readers as possible.

* Chapter 7 on "The Quantum Theory of Many-Electron Systems" was compiled by Professor John Midtdal after the death of Dr. Hylleraas.

CHAPTER 1

The Origin and Foundation of Quantum Theory

1. HEAT RADIATION

In the year 1900 Max Planck (1858–1947), when investigating the laws of heat radiation, discovered a new basic quantity in nature, the *quantum of action* or *Planck's constant*. No single discovery in physics has led to consequences comparable to those that can be drawn from the simple fact that such a quantum of action exists. The complex of theories comprised in the phrase *quantum theory* is based on this discovery. The quantum hypothesis or quantum theory is the indispensable basis for all modern atomic theory.

It is rather surprising that quantum theory should originate just from studies of heat radiation. The quantum of action might as well have been discovered in some other way, as for instance in connection with studies of *photoelectricity*. After the discovery of electromagnetic waves it was also plain to every physicist that heat radiation had to be considered an irregular mixture of all kinds of electromagnetic radiation. Why should a fundamental and simple law of nature be discovered in connection with such a complex process as heat radiation and not from some much simpler phenomenon? As to this question we shall only point to the historical fact, and instead of asking why we shall start our treatment of *quantum theory* by discussing the main feature of heat radiation.

As early as the 17th century Sir Isaac Newton (1642–1727) became interested in questions concerning heat radiation. He invented a rational scale of temperature which he applied to express his law of the cooling of bodies due to loss of heat by radiation.

It is a common experience that hot bodies are cooled down when placed in cooler surroundings. If there is little or no conduction of heat, this loss of heat must be due to radiation. Bodies also receive heat by radiation, particularly when placed in hotter surroundings. But a hot body takes up radiation even from cooler bodies. Accepting this simple fact and distinguishing between

radiant heat given out and taken up, we find that the laws of heat radiation become much simpler. On considering the heat radiation emitted from a body independent of its surroundings, closer examinations have led to the simple law that it is proportional to the fourth power of the absolute temperature T. By T we mean the temperature as expressed in the absolute thermodynamic or Kelvin scale of temperature.

In addition to the temperature the heat radiation depends on the physical properties of the body. Heat radiation is essentially of the same nature as optical light and consists of electromagnetic waves. Hence it is not sufficient to know the total amount of heat radiation. A complete description must also include the distribution of radiant energy on different wavelengths.

The dependence of heat radiation on wavelength may be very different for different bodies. This is a great complication. The first to bring an important simplification in this state of matter was Kirchhoff (1824–1887). In 1859 he announced his discovery that the ratio of emissive to absorptive power for radiation of any given wavelength was the same for all bodies.

On the basis of this discovery it is possible to construct a fictitious body with well-defined and highly important radiation properties. It is called a "perfectly black" body, or simply "black" body and can be defined by stating that it totally absorbs any radiation of heat or light falling upon it. Its absorbtive power, hence, is 1 for all wavelengths. Its emissive power, according to Kirchhoff's law, is a function only of temperature and wavelength. This function expresses a law of nature of the most general character, giving the ratio of emissive to absorptive power for all kinds of bodies. The theoretical deduction of this law, although for a long time encountered by apparently unsurmountable difficulties, finally led to one of the most brilliant discoveries ever made in physical research.

The concept of an ideal blackbody is inherently connected with another concept, that of pure *temperature* or *blackbody radiation*. Blackbody radiation at a given temperature T can be defined as the radiation around a body that is in thermodynamic equilibrium with its surroundings at the same temperature.

Definition of Blackbody Radiation

As a general rule dark bodies are the best absorbers of light. Hence, by Kirchhoff's law they must also give off more light and heat by radiation than lighter bodies. This sounds a bit curious because we are apt to think of light or shining bodies as particularly good radiators. Everyday experience tells us, however, that a bright and shining body is able to keep its warmth much better than a dark and dim one. The brilliant radiation from shining bodies does not come from their interior but is mainly due to reflected light.

In addition to the concept of the blackbody the concepts of a perfectly *white* and a perfectly *bright* or *shining* body have been introduced. The

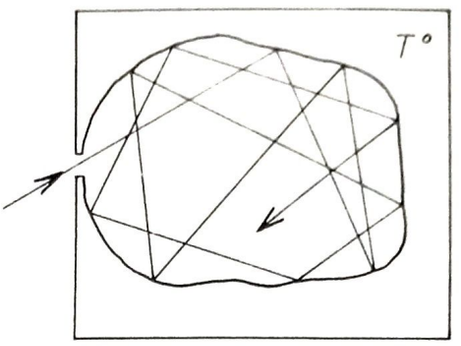

Fig. 1-1

absorptive power of these bodies is zero. They totally reflect all kinds of radiation. There is, however, a distinct difference in their way of reflecting. The shining body is considered to have a smooth surface, reflecting all radiation according to the well-known ordinary law of reflection. The surface of the white body, on the other hand, must be thought of as rough and thus reflects all kinds of light irregularly into all directions in space.

In everyday life a blackbody is obtained by covering a body's surface with some dark material as soot, or by painting it black. But this is only a poor substitute for an ideal blackbody. Even the apparently darkest bodies reflect appreciable radiation. An ideal blackbody can be realized only in an artificial manner. Consider, for instance, a fairly well absorbing material with an inside cavity. If this cavity is provided with a small opening for the passage of light and heat radiation, this aperture actually possesses the same properties as the surface of an ideal blackbody. Radiation entering through this opening is reflected a large number of times on the inside walls of the cavity and will have a practically negligible chance of leaving the cavity before total absorption. (See Fig. 1-1.) That this will be true even if the walls are absorbing moderately can be shown by a simple experiment. Two closed boxes with circular front apertures are differently painted inside, black and white. To a person looking simultaneously at the two apertures a difference in darkness is scarcely perceptible.

There can be no doubt that Kirchhoff's law applies also to this artificial model of a blackbody, the cavity; and its fictitious surface, the aperture. Another hypothesis would inevitably lead to absurdities. Hence the radiation emerging from the cavity through the aperture must have just the same qualities as the radiation from the surface of an ideal blackbody of the same temperature as the cavity and its walls.

The rate of radiation per unit area of the aperture and the density of radiation inside the cavity are uniquely related to each other. One can therefore define blackbody radiation as the radiation found in the cavity. Again this radiation will be the same as that found anywhere between a number of bodies, whether of equal or different material, provided that they are all kept at the same temperature. This uniform temperature is created by the radiation

itself for an isolated system simply by leaving it to reach thermal radiative equilibrium.

Connection between Radiation Density and Surface Luminosity or Brightness

For experimental measurements in pyrometry and astronomy one must know accurately the connection between the energy density of the radiation and the rate of emission of radiation from the surface of a blackbody. The rate of emission is usually expressed by the so-called surface brightness K_ν for the radiation of frequency ν. It is defined as the emission of radiation per unit time and unit area from the surface of the blackbody into a unit solid angle in a direction normal to the surface. According to the cosine law the corresponding emission in another direction making an angle ϑ with the normal to the surfaces will be $K_\nu \cos\vartheta$. The radiation received by a surface element dS at a distance r perpendicular to the direction of radiation from a surface element $d\sigma$ of the blackbody will thus be

$$d\sigma\, K_\nu \cos\vartheta \cdot \frac{dS}{r^2} = dS\, K_\nu\, d\Omega, \tag{1.1}$$

where r is the distance from dS to $d\sigma$, and $d\Omega$ is the solid angle which the surface element $d\sigma$ subtends at dS. (See Fig. 1-2.)

This explains why, for instance, the surface of the sun appears to us as a plane disk. The reduced radiation from the inclined surface elements near the edges is exactly compensated by the larger areas of the elements comprised within a given solid angle. From (1.1) we see that K_ν must be used, together with Stefan-Boltzmann's law (2.1), if we want to calculate, say, the temperature of the sun's surface from the solar constant (which is the amount of heat energy falling per sec on a unit area perpendicular to the directions of the sun's rays just outside the earth's atmosphere). The result of the calculation will be approximately the same as when the temperature is calculated from the wavelength at the energy maximum by Wien's displacement law (2.2).

As will be shown, the relation between radiation density $u(\nu)$ and surface brightness is

$$K_\nu = \frac{c}{4\pi} u(\nu), \tag{1.2}$$

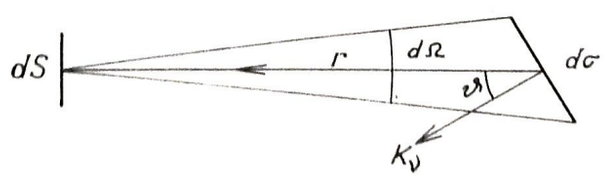

Fig. 1-2. Definition of surface brightness K_ν. $d\sigma K_\nu \cos\vartheta \dfrac{dS}{r^2} = dS\, K_\nu\, d\Omega$.

and between brightness and total emission E_ν per unit area of the surface

$$E_\nu = \pi K_\nu = \frac{c}{4} u(\nu). \tag{1.3}$$

(Sometimes the brightness is referred to each of the two main components of polarization, in which case we have to put $K_\nu = \mathrm{cu}(\nu)/8\pi$.)

The relation (1.2) between K_ν and $u(\nu)$ can be found in different ways. A very simple procedure is to imagine the radiation distributed between three main directions normal and parallel to the surface. The total emission would then apparently be $\mathrm{cu}(\nu)/6$ which is not a correct result. However, the component of momentum of radiation normal to the surface, which is c times smaller, will be

$$p = \frac{u(\nu)}{6}. \tag{1.4}$$

Now the emission of radiation per unit area and unit solid angle in a direction with polar angle ϑ is $K_\nu \cos\vartheta$. Hence the component of momentum in a normal direction is found by dividing by c and multiplying by $\cos\vartheta$ and $d\Omega$. In this way we obtain the relation

$$\frac{1}{6} u(\nu) = \frac{1}{c} K_\nu \int \cos^2\vartheta \, d\Omega. \tag{1.5}$$

For a half-sphere $\overline{\cos^2\vartheta} = \frac{1}{3}$, and the total solid angle is 2π. From this we get the relation (1.2). In a similar way we find, since $\overline{\cos\vartheta} = \frac{1}{2}$ for a half-sphere,

$$E_\nu = K_\nu \int \cos\vartheta \, d\Omega = \pi K_\nu, \tag{1.6}$$

which is the same as (1.3).

Problems

1. A surface element normal to the direction of radiation is receiving an amount of radiation $K_\nu \, d\Omega$ per unit area and unit time from a radiating body subtending a solid angle $d\Omega$. What is the volume density of radiation near to the surface element due to this radiating body? What is the density of radiation at the center of a sphere with uniformly radiating walls?
2. Consider a cavity with surrounding walls of arbitrary shape and constant surface brightness K_ν. What is the volume density $u(\nu)$ of a radiation with frequency ν at any point of the cavity?
3. Consider a very small body inside an enclosure filled with radiation. The radiation absorbed by the body may be considered negligible compared to the total radiation penetrating it. Call the surface brightness per unit frequency of the body

K_ν. This quantity then necessarily will be equal to the inside brightness of a sphere surrounding the body and representing incoming radiation. Show that the absorbed energy per unit volume of the body and per unit time and unit frequency range is

$$4\pi a_\nu K_\nu,$$

where a_ν is the absorption coefficient. On the other hand, if e_ν is the emission coefficient referred to unit solid angle and unit frequency range, the corresponding emitted energy per unit volume and unit time is

$$4\pi e_\nu.$$

Putting the two quantities equal, we get a mathematical expression for Kirchhoff's law

$$K_\nu = \frac{e_\nu}{a_\nu}.$$

2. QUANTITATIVE LAWS FOR BLACKBODY RADIATION

The Stefan-Boltzmann Law. The Wien Displacement Law

Before considering the characteristic features of blackbody radiation from a purely theoretical point of view, it may be useful to look for conclusions that can be drawn from experimental physical measurements.

As already mentioned, the total radiation from a heated body is proportional to the fourth power of its absolute temperature. This law is necessarily valid not only for the emission of radiation from a blackbody; owing to the proportionality between the emission and radiation density inside the cavity representing the blackbody, the law will hold also for the energy density in blackbody radiation. If we write $u(T)$ for this energy density, we must have

$$u(T) = aT^4, \tag{2.1}$$

where a is a universal constant. The law is usually named *the Stefan-Boltzmann law* with reference to J. Stefan (1835–1893), who made the first decisive quantitative measurements (published in 1879), and to L. Boltzmann (1844–1906), who was able to give a theoretical derivation of the law.

Another important law found by W. Wien (1864–1928) is known as *Wien's displacement law*. The radiation from a black body at a given temperature T will have an energy maximum at a definite wavelength λ_m. This maximum is displaced toward shorter wavelengths with increasing temperature according to the law

$$\lambda_m T = b, \tag{2.2}$$

where b is another fundamental constant. This important law has proved to be an indispensable aid in both pyrometry for the determination of the

temperatures of incandescent bodies, and in astronomy for measurements of the surface temperature of astronomical objects.

General Character of Temperature Radiation

We shall use these two fundamental experimental laws to derive a more general law governing the spectral distribution of energy in blackbody radiation, assuming the two laws to be perfectly correct. This of course cannot be definitely proved by experiments but only from more extended theoretical considerations.

We shall write $u(\nu, T)$ [or sometimes $u(\nu)$] for the energy density per unit frequency interval of radiation,

$$u(T) = \int_0^\infty u(\nu, T)\, d\nu. \tag{2.3}$$

The energy density per unit wavelength interval can also be used. This is a slightly different function which we denote by $\rho(\lambda, T)$,

$$u(T) = \int_0^\infty \rho(\lambda, T)\, d\lambda. \tag{2.4}$$

Using the relation $\lambda\nu = c$ (λ = vacuum wavelength), c being the velocity of light that is common to all kinds of electromagnetic waves, we get the general relation

$$u(\nu, T) = \rho(\lambda, T) \cdot \left(-\frac{d\lambda}{d\nu}\right) = \frac{c}{\nu^2}\rho(\lambda, T) \tag{2.5}$$

between the two functions $u(\nu)$ and $\rho(\lambda)$.

Wien's displacement law now permits us to write

$$\frac{\partial \rho}{\partial \lambda} = 0 \qquad \text{for} \qquad \lambda T = b. \tag{2.6}$$

Introducing in addition the new variable $x = \lambda T$ and expressing ρ as a function $\rho(x, T)$ of x and T, we have

$$\frac{\partial \rho}{\partial x} = 0 \qquad \text{for} \qquad x = b. \tag{2.7}$$

On considering this equation valid for any value of T it should be legitimate to write

$$\rho = f(x)g(T), \qquad f'(b) = 0, \tag{2.8}$$

Here $f(x)$ and $g(T)$ are both general functions. Inserting ρ in (2.4) and comparing with the Stefan-Boltzmann law $u(T) = aT^4$, we see that $g(T) = \text{const}\ T^5$. Multiplying and dividing $g(T)$ simultaneously by the factor λ^5 and

putting the factor $(\lambda T)^5$ into the general function of $x = \lambda T$, we can write the energy density per unit wavelength as

$$\rho(\lambda, T) = \frac{1}{\lambda^5} G(\lambda T). \tag{2.9}$$

From this equation and (2.5), together with $\lambda\nu = c$, we easily obtain the form

$$u(\nu, T) = \nu^3 F\left(\frac{\nu}{T}\right) \tag{2.10}$$

for the energy density per unit frequency.

Problem

1. Show that the more general expression for (2.8), $\rho = f_1(x)g_1(T) + f_2(x)g_2(T) + \cdots$ necessarily leads to $c_1 g_1(T) = c_2 g_2(T) = \cdots$, and, hence, that (2.8) is the general expression.

3. PLANCK'S RADIATION LAW

Electromagnetic Eigenvibrations of a Cavity

Among the theories proposed before the establishment by Planck of the correct radiation law we shall note two laws known as the *Rayleigh-Jeans law* and *Wien's law*. The first one can be written

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} kT. \tag{3.1}$$

It is easily seen to have the general form given in (2.10). The quantity k, called Boltzmann's constant, was introduced by Boltzmann in his statistical-mechanical definition of entropy. It also appears in the Boltzmann distribution law for thermodynamic equilibrium.

Later on we shall give a more rigorous derivation of the numerical factor in the Rayleigh-Jeans law. For the time being we shall content ourselves with a plausible argument for the law which runs as follows. Consider the electromagnetic scalar wave equation

$$\nabla^2\Phi = \frac{1}{c^2}\frac{\partial^2\Phi}{\partial t^2}, \tag{3.2}$$

and the amplitude equation for waves with frequency ν

$$\nabla^2\Phi + \left(\frac{2\pi\nu}{c}\right)^2\Phi = 0. \tag{3.3}$$

In a cavity with smoothly reflecting walls, say, with the boundary condition $\Phi = 0$ and for simplicity in the form of a cube with sidelength a, the eigenoscillations will have the form

$$\Phi = \sin \pi \frac{lx}{a} \sin \pi \frac{my}{a} \sin \pi \frac{nz}{a}, \tag{3.4}$$

l, m, and n being positive integers. According to (3.3) the possible frequencies are related to these numbers by the equation

$$\left(\frac{2\nu a}{c}\right)^2 = l^2 + m^2 + n^2 = L^2. \tag{3.5}$$

The number of eigenvibrations in a given range of frequency may be calculated as follows. Representing the three numbers l, m, and n by the points of a unit cubic lattice, the number of points in a given range is equal to the volume of this range in the space of the cubic lattice. In such calculations we usually have to consider the volume between two spheres of radii L and $L + dL$. In the above case we need only consider positive values of the integers l, m, and n, since according to (3.4) a change of sign for any one of them leads to the same solution as for the positive value. Hence we have to deal merely with the positive octant of the lattice. This volume is

$$\frac{\pi}{2} L^2 \, dL = \frac{4\pi a^3}{c^3} \nu^2 \, d\nu. \tag{3.6}$$

Considering that the electromagnetic waves are transverse waves, which must be characterized also by two independent states of polarization, we infer that the number of possibilities for standing waves is doubled. To obtain the true number of possible eigenvibrations we must therefore double expression (3.6). Dividing also by the volume a^3 of the cavity, we may therefore take the number of vibrations per unit frequency and unit volume to be

$$\frac{8\pi\nu^2}{c^3}. \tag{3.7}$$

Each of these eigenvibrations can now formally be treated as a harmonic oscillator. According to classical statistical mechanics the oscillator will acquire a mean kinetic energy kT when placed in surroundings of temperature T and left to obtain thermodynamic equilibrium with the surroundings. The multiplication of (3.7) by this mean energy yields an energy density of the cavity corresponding to the Rayleigh-Jeans law of (3.1).

The Rayleigh-Jeans and Wien Radiation Laws

The Rayleigh-Jeans law agrees with observation at moderate temperatures in the low frequency (or long wavelength) region as well as at high temperature in the moderate frequency region. For any given wavelength the formula

will be fairly accurate provided that the temperature is sufficiently high. As a general law for all wavelengths it is absurd, however, since it leads to an infinitely high value of the total energy density $u(T)$.

It is possible to avoid this difficulty by presupposing an exponentially decreasing radiation function for large ν, or rather for large ν/T, as for instance,

$$u(\nu, T) = \text{const } \nu^3 e\left(-C\frac{\nu}{T}\right)^{1/2}. \tag{3.8}$$

This formula, which was proposed by W. Wien and is sometimes called Wien's radiation formula, must not be confused with his displacement law. In contrast to the Rayleigh-Jeans law, Wien's formula can be brought into agreement both with the Stefan-Boltzmann law and with Wien's displacement law. The two constants in formula (3.8) are then determined by the experimental values of a and b in (2.1) and (2.2). The weakness of Wien's radiation law is that it fails to account satisfactorily for the radiation density at smaller frequencies because it does not agree with the Rayleigh-Jeans law as $\nu \to 0$ or $T \to \infty$.

The correct radiation law was found by Max Planck in the year 1900. It was originally based on some particular considerations combined with a bold speculation. It reads

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{h\nu/(e^{kT} - 1)}, \tag{3.9}$$

h being a new fundamental constant of the dimension of energy times time, which is also called action. For this reason it has been given the name *quantum of action.* It is also called Planck's constant.

If $\nu/T \to 0$, the denominator of (3.9) can be replaced by $h\nu/kT$. Hence Planck's formula agrees with the Rayleigh-Jeans law for small frequencies and large wavelengths. On the other hand, it also conforms with Wien's radiation law in the region in which this law is valid, that is, if $\nu/T \to \infty$. In order that the Planck radiation law shall agree with the Stefan-Boltzmann law and Wien's displacement law, we must assign appropriate values to the two constants h and k. If this is done, the law is in complete agreement with observations in the whole frequency spectrum of blackbody radiation for any value of the temperature.

Calculation of Numerical Values of h and k

Applying the Planck formula (3.9) to the Stefan-Boltzmann law and the displacement law, we see that it is possible to deduce the following relations

between h and k and the experimental constants a and b:

$$a = 8\pi k\left(\frac{k}{hc}\right)^3 \cdot \frac{\pi^4}{15}, \qquad \left(\frac{\pi^4}{15} = \int_0^\infty \frac{x^3\,dx}{e^x - 1}\right),$$
$$b = \frac{hc}{kx}, \qquad x = 4.965, \tag{3.10}$$

x being defined by the equation

$$x = 5(1 - e^{-x}). \tag{3.11}$$

Solving equation (3.10) with respect to h and k, we find

$$k = \frac{15a}{8\pi^5} \cdot \left(\frac{b}{x}\right)^3, \qquad h = \frac{15a}{8\pi^5 c}\left(\frac{b}{x}\right)^4. \tag{3.12}$$

With the values of a and b as measured by Lummer and Pringsheim, Paschen, Warburg, and Müller,

$$a = 7.64 \cdot 10^{-15}\ \text{erg/cm}^3\ \text{deg}^4, \qquad b = 0.288\ \text{cm/deg}, \tag{3.13}$$

we obtain the following values of h and k:

$$h = 6.525 \cdot 10^{-27}\ \text{erg sec}, \qquad k = 1.369 \cdot 10^{-16}\ \text{erg/deg}. \tag{3.14}$$

According to the latest investigations by R. T. Birge, based on the most reliable experimental measurements in various fields of physics, the most probable values of h and k and a number of other closely related physical constants are

$$\begin{aligned} h &= (6.624 \pm 0.002) \cdot 10^{-27}\ \text{erg sec}, \\ k &= (1.38047 \pm 0.00026) \cdot 10^{-16}\ \text{erg/deg}, \\ R &= (8.31436 \pm 0.00038) \cdot 10^{7}\ \text{erg/deg}, \end{aligned} \tag{3.15}$$

$$\begin{aligned} F &= (96{,}514 \pm 10)\ \text{coulomb}, \\ N &= (6.0228 \pm 0.0011) \cdot 10^{23}, \\ e &= (4.8025 \pm 0.0010) \cdot 10^{-10}\ \text{deg/e.s.u.} \end{aligned} \tag{3.16}$$

Recalculating the most probable values of the radiation constants a and b in the Stefan-Boltzmann law and Wein's distribution law, we find

$$\begin{aligned} a &= 7.5703 \cdot 10^{-15}\ \text{erg/cm}^3\ \text{deg}^4 \\ b &= 0.2897\ \text{cm deg}. \end{aligned} \tag{3.17}$$

Problems

1. Show that the Planck radiation law can be expressed as

$$\rho(\lambda, T) = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda cT} - 1}.$$

Prove by differentiation with respect to λ that, for a given T the maximum intensity is formed at a wavelength λ, where $b = \lambda T = hc/kx$, $x = 5(1 - e^{-x})$. Put $x = 5$ in the exponential function and calculate the corresponding approximate value of x.

2. Put $h\nu/kT = x$ in the Planck formula (3.9) and calculate the total energy density by expanding $1/(e^x - 1)$ in powers of e^{-x}. Show that the result is equivalent to the first equation of (3.10) if

$$\frac{\pi^4}{15} = 6\left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \cdots\right).$$

3. Remembering that the gas molar constant $R \approx 2$ cal/centigrade and that 1 cal $\approx 4.186 \cdot 10^7$ erg, show that from $N = R/k$ we get a reasonable value of the Avogadro number N.
4. Take the electrochemical constant $F = 96{,}540$ coulombs. Show that from this value we get a reasonable value for the electronic charge e.

4. THE CHARACTERISTICS OF TEMPERATURE RADIATION AS DEDUCED FROM THERMODYNAMIC AND ELECTRODYNAMIC LAWS

Thermodynamics of Radiation

The theoretical deduction of the Stefan-Boltzmann law is comparatively easy. In addition to the first and second law of thermodynamics we need only the well-known formula for the radiation pressure

$$P = \tfrac{1}{3}u. \tag{4.1}$$

exerted by isotropic radiation on material boundaries. Because of this relation the blackbody radiation, being a mixture of electromagnetic waves, will in several respects behave like a gas.

To study these gas properties consider an amount of radiation enclosed in a cylinder provided with a movable piston (Fig. 1-3). To begin with, let the cylinder be kept at a constant or approximately constant temperature by means of a heat bath, and let the walls be perfectly "black" in order to facilitate absorption and reemission of radiation by the walls. The piston is moved at a sufficiently slow rate so as to allow for reversibility of the whole process corresponding to thermodynamic equilibrium of the radiation. If V is the volume of the cylinder, the radiation energy is $U = u(T)V$. According to the first law of thermodynamics the amount of heat energy transferred to the radiation by a change of volume dV is

$$\delta Q = dU + P\,dV = V\,du + \tfrac{4}{3}u\,dV. \tag{4.2}$$

The corresponding change of entropy is

$$dS = \frac{\delta Q}{T} = \frac{V}{T}\frac{du}{dT}\,dT + \frac{4}{3}\frac{u}{T}\,dV, \tag{4.3}$$

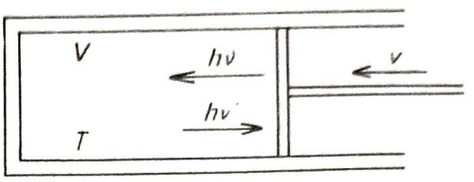

Fig. 1-3. Isothermal and adiabatic compression of radiation.

using T and V as independent thermodynamic variables and remembering that $u = u(T)$ depends upon T only. According to the second law of thermodynamics the entropy $S = S(T, V)$ is a single-valued function of two state variables. Hence from the two first-order derivatives of S as given by (4.2) we may calculate the second-order derivative $\partial^2 S/\partial T\,\partial V$ in two different ways

$$\frac{\partial S}{\partial T} = \frac{V}{T}\frac{du}{dT}, \qquad \frac{\partial S}{\partial V} = \frac{4}{3}\frac{u}{T},$$

$$\frac{\partial^2 S}{\partial T\,\partial V} = \frac{1}{T}\frac{du}{dT} = \frac{4}{3}\frac{1}{T}\frac{du}{dT} - \frac{4}{3}\frac{u}{T^2}.$$

The last equation yields

$$T\frac{du}{dT} = 4u, \qquad u(T) = aT^4, \tag{4.4}$$

where a is a universal constant. This is the Stefan-Boltzmann law. Inserting $u(T)$ in (4.3), we obtain in addition the entropy

$$S = \tfrac{4}{3}aT^3V + \text{const.} \tag{4.5}$$

To obtain the more general radiation law (2.10), which is also called Wien's radiation law, we must refer to an additional principle from pure electrodynamics, namely, the *Doppler principle*

$$\nu = \nu'\left(1 + 2\frac{v}{c}\cos\vartheta\right). \tag{4.6}$$

The meaning of this equation is that radiation of frequency ν' reflected from a moving body with velocity v normal to its surface changes its frequency into ν as given by (4.6) where ϑ is the angle of incidence.

Modification of Frequency due to the Doppler Effect

Suppose now the cylinder to be provided with perfectly "white" instead of "black" walls in order that no radiation may enter or leave the cylinder by heat transport. On the other hand, the diffuse reflection from the white walls ensures that the radiation remains isotropic and even conserves its character of pure blackbody radiation. If necessary we may imagine small, absorbing dust particles to be left in the cylinder in order to smooth out any deviation from the wavelength distribution of blackbody radiation which might possibly be caused by the moving piston.

If the motion of the piston is sufficiently slow, we now have an adiabatic process in the thermodynamic sense. Hence $dS = 0$, $S = \text{const}$, and according to (4.5)

$$T^3V = \text{const} \qquad \text{or} \qquad 3\frac{dT}{T} = -\frac{dV}{V}. \tag{4.7}$$

On the other hand, the energy of the enclosed radiation is changed by the amount

$$d(uV) = V\frac{du}{dT}\,dT + u\,dV = \left(u - \frac{1}{3}T\frac{du}{dT}\right)dV.$$

The corresponding change in energy in the frequency range from ν to $\nu + d\nu$ is

$$d\nu\, d(u(\nu)V) = d\nu\left(u - \frac{1}{3}T\frac{du(\nu)}{dT}\right)dV. \tag{4.8}$$

This increase of energy originates merely from the work performed in compressing the radiation by the moving piston.

We shall now investigate how the frequency of the radiation, and hence its frequency distribution, is changed owing to the Doppler effect produced by the moving piston. In this situation it may be of some advantage to imagine the radiation to consist of photons, since within an enclosure of white walls the photons cannot disappear but can only change their energy.

At normal reflection from the piston the frequency of a photon is changed, say, from ν' to

$$\nu = \left(1 + 2\frac{v}{c}\right)\nu'. \tag{4.9}$$

For photons within a given range $d\nu'$ it should be remembered that the change in frequency range is proportional to

$$d\nu = \left(1 + 2\frac{v}{c}\right)d\nu' = \frac{\nu}{\nu'}\,d\nu'. \tag{4.10}$$

Hence the frequency range is increased in the same ratio as the photon energy, that is, $h\nu : h\nu'$.

Initially the change of momentum is, of course, in the direction of the axis of the cylinder. The white walls, however, automatically spread the momentum gain in that direction over all directions in space. For this reason it is legitimate for the purpose of calculating the gain of momentum and kinetic energy to consider one-third of the photons moving in each of the directions of three main axes, one-sixth in the positive and one-sixth in the negative direction.

To facilitate the considerations further, take a time interval dt and a corresponding change of volume for which on the average each photon suffers one collision with the piston. For photons moving strictly along the axis of the cylinder this time would be $2L/c$, L being the length of the enclosure. Since only one-third of the photons are moving in this direction we must, however, take the three times larger time interval $6L/c$. The change of volume during this time interval is

$$dV = -\frac{6L}{c} qv = -\frac{6v}{c} V, \tag{4.11}$$

q being the area and v the velocity of the piston.

Because of the Doppler effect an amount of energy $V\,dvu(\nu, T)$ will disappear from the energy range between ν and $\nu + d\nu$ during this time. As a compensation new energy is entering this range, after having left the frequency range between ν' and $\nu' + d\nu'$. The magnitude of this energy before collision was $V\,d\nu' u(\nu', T)$. After the collision it will have increased to

$$V \frac{\nu}{\nu'} d\nu' u(\nu', T) = V\, d\nu u(\nu', T). \tag{4.12}$$

Hence for the interval $d\nu$ the gain of energy is

$$V\, d\nu[u(\nu', T) - u(\nu', T)] = V\, d\nu(\nu' - \nu)\frac{\partial u}{\partial \nu}$$

or, according to (4.9) and (4.11),

$$-d\nu\, V \cdot \frac{2v}{c} \cdot \nu \frac{\partial u}{\partial \nu} = d\nu\, dV \frac{1}{3} \nu \frac{\partial u}{\partial \nu}. \tag{4.13}$$

Putting this expression equal to the adiabatic change of energy as given by (4.8), we obtain

$$\frac{1}{3}\left(\nu \frac{\partial u}{\partial \nu} + T \frac{\partial u}{\partial T}\right) = u, \tag{4.14}$$

which is precisely the partial differential equation for the function $u = \nu^3 F(\nu/T)$.

Problems

1. A photon is moving in a direction ϑ to the normal of the piston and hence has one collision with the piston in each time interval $2L/c \cos \vartheta$. How much energy will it gain from the piston in one collision, and how much will be the mean gain for photons distributed uniformly over all directions ϑ?

5. RADIATION AND MATTER IN THERMODYNAMIC EQUILIBRIUM

Mean Radiation from an Electric Oscillator

In (3.7) we found a relation between the radiation density and the mean energy of an oscillator at a temperature T on the supposition that each electrodynamic eigenvibration of an enclosure could be represented by a harmonic oscillator of the same frequency. We shall now deduce this relation in a more direct and intelligible way.

In studying radiation in thermodynamic equilibrium with the surrounding matter we are free to choose as simple and convenient models as we like for material particles. Owing to the universal nature of temperature radiation its frequency distribution does not depend on the sort of atoms or molecules with which it is exchanging energy. Accordingly we may use the simplest conceivable mechanical model which is the linear or, eventually, the spatial harmonic oscillator. The oscillating particle must, however, have an electric charge e in order to be influenced by the electric oscillations of the radiation field.

Let each of the oscillators have a mass m and let their frequencies $\nu = \omega/2\pi$ be distributed with sufficient density over the whole frequency range $0 \leq \nu \leq \infty$. The intensity of radiation emitted from one of the oscillators is known from electrodynamic considerations to be

$$\eta_e = \frac{\omega^4 e^2 a^2}{3c^3} = \frac{2\omega^2 e^2}{3mc^3} W, \tag{5.1}$$

W being the mechanical energy of the oscillator. In this equation the rate of emission η_e can be replaced by its mean value $\overline{\eta}$ if W is replaced by its mean value $\overline{W}$.

Absorption of Energy from the Radiation Field

If the electric field of the temperature radiation at any point in space is resolved into Fourier components with frequencies $\nu_n = \omega_n/2\pi$, we get

$$\mathbf{E} = \sum_n (\mathbf{A}_n \cos \omega_n t + \mathbf{B}_n \sin \omega_n t). \tag{5.2}$$

This resolution can always be performed for a limited time interval $0 \leq t \leq T$ if we choose $\Delta\nu = \nu_{n+1} - \nu_n = 1/T$ for the successive frequencies of the Fourier series.

The Fourier components $\mathbf{A}_n$ and $\mathbf{B}_n$ will vary irregularly from time to time and from one point to another in space. Hence averaging over a great number of oscillators of the same frequency, we shall always have $\overline{\mathbf{A}_n \mathbf{B}_n} = 0$;

however, $\overline{\mathbf{A}_n^2} = \overline{\mathbf{B}_n^2} > 0$. When averaging over a great many oscillators, products of the first kind can be left out. Of course, we also have $\mathbf{A}_n\mathbf{B}_n = 0$, but this is irrelevant since such products yield zero when averaged over time.

From the mechanical theory of forced oscillations we already know the solutions for a three-dimensional harmonic oscillator with frequency $\nu = \omega/2\pi$. If $\mathbf{r}$ is the space vector of the oscillator and $\mathbf{E}$ the electric field vector, the equation of motion reads

$$\ddot{\mathbf{r}} + \omega^2\mathbf{r} = \frac{e}{m}\mathbf{E}. \tag{5.3}$$

If the initial condition for the oscillator at time $t = 0$ is given by $\mathbf{r} = \mathbf{a}$, $\dot{\mathbf{r}} = \mathbf{b}$, we find on introducing the expression (5.2) for $\mathbf{E}$

$$\mathbf{r} = \mathbf{a}\cos\omega t + \frac{\mathbf{b}}{\omega}\sin\omega t + \sum_n \frac{e}{m(\omega^2 - \omega_n^2)} \times \left[\mathbf{A}_n(\cos\omega_n t - \cos\omega t) + \mathbf{B}_n\left(\sin\omega_n t - \frac{\omega_n}{\omega}\sin\omega t\right)\right]. \tag{5.4}$$

As the initial conditions must also be considered to be distributed at random it is legitimate to assume $\overline{\mathbf{aA}_n} = 0$, $\overline{\mathbf{aB}_n} = 0$, and so forth. In computing the space and time averages of the absorption

$$\bar{\eta}_a = \frac{1}{T}\int_0^T \overline{e\mathbf{E}\dot{\mathbf{r}}}\, dt \tag{5.5}$$

we are therefore justified in disregarding all kinds of cross products. Moreover, owing to the averaging in time, we are also allowed to disregard products like $\cos\omega_n t \sin\omega_n t$ and $\cos\omega t \sin\omega t$. We must, however, take care of products like $\cos\omega t \sin\omega_n t$, and so on, if ω_n is very near to ω. Leaving aside all kinds of products as discussed above, (5.5) can be reduced to the following fairly simple form

$$\bar{\eta}_a = \frac{1}{T}\int_0^T \overline{e\mathbf{E}\dot{\mathbf{r}}}\, dt = \sum_n \frac{1}{T}\int_0^T dt \cdot \frac{e^2}{m(\omega^2 - \omega_n^2)} \cdot \cdot \overline{(\mathbf{A}_n^2\omega\cos\omega_n t\sin\omega t - \mathbf{B}_n^2\omega_n\sin\omega_n t\cos\omega t)}$$

$$= \sum_n \frac{e^2\overline{\mathbf{A}_n^2}}{2m} \cdot \frac{1}{T}\int_0^T \left(\frac{\sin(\omega - \omega_n)t}{\omega - \omega_n} + \frac{\sin(\omega + \omega_n)t}{\omega + \omega_n}\right) dt. \tag{5.6}$$

For values of T corresponding to a large number of oscillations the second term in the integral is insignificant and we may write

$$\bar{\eta}_a = \sum_n \frac{e^2\overline{\mathbf{A}_n^2}}{2m} \cdot \frac{1 - \cos(\omega - \omega_n)T}{(\omega - \omega_n)^2 T}. \tag{5.7}$$

We now clearly see that the main contribution to the absorption comes from the neighborhood of $\omega_n = \omega$. Consequently the factor $\overline{\mathbf{A}_n^2}$, which may be considered to vary only slowly with n, may be taken outside the sign of summation and put equal to its value for $\omega_n = \omega$. On the other hand, the mean value of $\overline{\mathbf{E}^2}$ is

$$\overline{\mathbf{E}^2} = \sum_n \overline{\mathbf{A}_n^2}, \tag{5.8}$$

and

$$4\pi\bar{u} = \tfrac{1}{2}(\overline{\mathbf{E}^2} + \overline{\mathbf{H}^2}) = \overline{\mathbf{E}^2}$$

$$= 4\pi \sum_n u(\nu_n, T)\,\Delta\nu_n = 2\sum_n u(\nu_n, T)\,\Delta\omega_n. \tag{5.9}$$

Since $\Delta\omega_n = 2\pi/T \to 0$ as $T \to \infty$, $\overline{\mathbf{A}_n^2}$ is to be replaced by $2u(\nu, T)\,d\omega$ when passing from a sum to the corresponding integral. Introducing the auxiliary variable $x = (\omega - \omega_n)T$, we get from (15.6)

$$\bar{\eta}_a = \frac{e^2 u(\nu, T)}{m} \int_{-\infty}^{\infty} \frac{1 - \cos x}{x^2}\, dx = \frac{\pi e^2 u(\nu, T)}{m}. \tag{5.10}$$

If there is to be thermodynamic equilibrium between radiation and matter, the mean absorption and mean emission of the oscillators must balance. It should be kept in mind, however, that η_e in (5.1) is valid only for a single linear harmonic oscillator, whereas our spatial model used in the computation of absorption is equivalent to three linear oscillators. Hence we should put as equilibrium condition

$$\bar{\eta}_a = 3\bar{\eta}_e. \tag{5.11}$$

From (5.1) and (5.9) we then obtain

$$u(\nu, T) = \frac{2\omega^2}{\pi c^3}\,\overline{W} = \frac{8\pi\nu^2}{c^3}\,\overline{W}, \tag{5.12}$$

which is the same formula as already found by counting the number of electromagnetic eigenvibrations per frequency interval in a cavity.

6. CONSEQUENCES OF THE QUANTUM THEORY FOR HEAT RADIATION

Classical Mean Thermal Energy of an Oscillator

The problem of determining theoretically the general radiation function $u(\nu, T)$ is now reduced to the computation of the mean thermal energy of an oscillator. From classical statistical mechanics we already know the solution

of this problem. The state of a linear harmonic oscillator can be indicated by a point in the two-dimensional phase space of the coordinate q and the momentum p of the oscillator. Its energy is given by the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{m}{2}\omega^2 q^2, \qquad \omega = 2\pi\nu, \tag{6.1}$$

ν being the mechanical frequency of the oscillator.

According to the principles of statistical mechanics the mean total energy of a system that is in thermodynamic equilibrium with its surroundings can be found from the Boltzmann distribution law by assigning a statistical weight $e^{-E/kT}$ to each state of energy E. Representing each state by an infinitely small area $dq\,dp$ in the (q, p)-plane, we find that the mean energy value of the oscillator is

$$\overline{W} = \frac{\iint_{-\infty}^{\infty} He^{-H/kT}\,dq\,dp}{\iint_{-\infty}^{\infty} e^{-H/kT} dq\,dp}. \tag{6.2}$$

By means of the well-known integrals

$$\int_{-\infty}^{\infty} e^{-x^2/\beta}\,dx = \sqrt{\pi\beta}, \qquad \int_{-\infty}^{\infty} e^{-x^2/\beta}\,x^2\,dx = \frac{1}{2}\beta\sqrt{\pi\beta} \tag{6.3}$$

we find

$$\overline{W} = \frac{(2\pi/\omega)(kT)^2}{2\pi/\omega(kT)} = \frac{1/\nu\,(kT)^2}{1/\nu\,(kT)} = kT. \tag{6.4}$$

We can, however, simplify the calculations in a convenient way by dividing the phase space into cells between curves of constant energy $H = E$. This simply means that we are transforming the double integrals of (6.2) by taking the energy E as one of the "coordinates" in phase space. The other natural coordinate, orthogonal to E, is then the time t which is the canonical conjugate to E.

From (6.1) we see that the maximum values of q and p are $(2E/m\omega^2)^{1/2}$ and $(2mE)^{1/2}$, respectively. The relations between q, p and E, t therefore are

$$q = \left(\frac{2E}{m\omega^2}\right)^{1/2} \sin\omega t, \qquad p = (2mE)^{1/2}\cos\omega t \tag{6.5}$$

or

$$t = \frac{1}{\omega}\arctan\frac{m\omega q}{p}. \tag{6.6}$$

Hence the functional determinant is

$$\frac{\partial(q, p)}{\partial(t, E)} = \begin{vmatrix} \frac{\partial q}{\partial t} & \frac{\partial q}{\partial E} \\ \frac{\partial p}{\partial t} & \frac{\partial p}{\partial E} \end{vmatrix} = \begin{vmatrix} \frac{p}{m} & \frac{q}{2E} \\ -\omega^2 mq & \frac{p}{2E} \end{vmatrix} = 1 \tag{6.7}$$

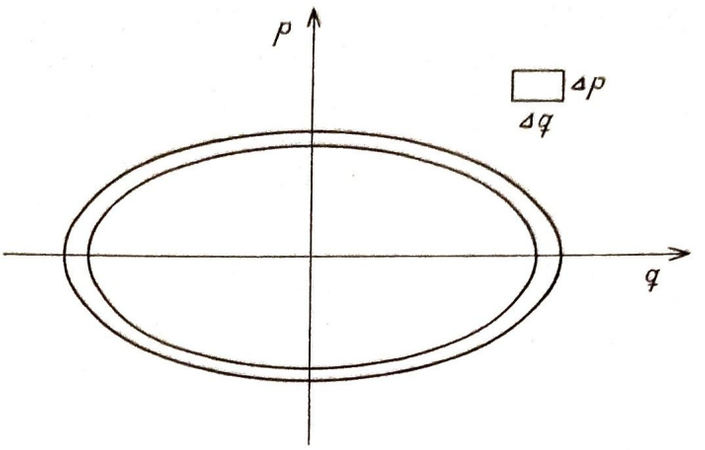

Fig. 1-4. Phase cells $\Delta q\,\Delta p$ and $\Delta t\,\Delta E$ (elliptic ring) for a harmonic oscillator.

which proves that the elementary cell $dq\,dp = dt\,dE$ is unaltered by the transformation (6.5).

As the energy is independent of t we may integrate t over a period from $t = 0$ to $t = 2\pi/\omega = 1/\nu$. An interval of ΔE in E will then form an elliptic ring as shown in Fig. 1-4. Integration in t yields merely a factor of $1/\nu$ which is the same factor as in (6.4).

On dropping this factor, the result is

$$\overline{W} = \frac{\int_0^\infty E e^{-E/kT}\,dE}{\int_0^\infty e^{-E/kT}\,dE} = \frac{(kT)^2}{(kT)} = kT \tag{6.8}$$

as before. The calculation, however, is much simpler.

Mean Energy According to Quantum Theory

So far we have considered phase cells infinitely small. The whole quantum theory could, however, be based upon a fundamental postulate which states that the phase cells are finite and of magnitude $\Delta q\,\Delta p = h$. If we take as a phase cell a time interval $\Delta t = 1/\nu$ corresponding to a full period and an energy breadth ΔE, the area or "volume" of the phase cell is

$$\Delta t\,\Delta E = \frac{\Delta E}{\nu}. \tag{6.9}$$

If this volume is put equal to h, the energy of the oscillator is divided into intervals of magnitude

$$\Delta E = h\nu. \tag{6.10}$$

Both the older and the new quantum theory tell us that an atomic model like the harmonic oscillator has sharply defined energy levels. If these levels are placed in the middle of the above phase cells, the "quantized" energy values will be

$$E_n = (n + \tfrac{1}{2})h\nu. \tag{6.11}$$

These are the energy levels which are found by wave-mechanical methods. The quantity $\frac{1}{2}h\nu$ for the ground state is the so-called "zero-point" energy. The older Bohr quantum theory, being more intuitive than the present theory, did not consider these peculiarities and simply assigned the values $E_n = nh\nu$ to the stationary states of the harmonic oscillator.

If the zero-point energy is retained in the formula for E_n, it will give a corresponding additional term $\frac{1}{2}h\nu$ in the mean oscillator energy $\overline{W}$. Such a procedure, when applied to the above problem, leads to a formula that is different from Planck's radiation law. At low temperatures and high frequencies the term $\frac{1}{2}h\nu$ will cause considerable deviation from experimental measurements. Hence one would be inclined to drop this term without any further explanation, leaving the question for more advanced speculations.

If, however, we are computing one part of the problem by means of wave mechanics we should also apply wave-mechanical considerations in treating other aspects of the same problem. According to wave mechanics the rate of emission of radiation from an oscillator is proportional to the square of a so-called matrix element. This matrix element, corresponding to a transition from a state n to a state $n - 1$, is again proportional to the mean energy of the two states and not to any of the energies of the separate states; that is, it is proportional to

$$E_n' = \tfrac{1}{2}(E_n + E_{n-1}) = nh\nu. \tag{6.12}$$

This is, although in a different sense, the formula of the older quantum theory; it shows that, at least with respect to radiation problems, it is as natural to relate our considerations to these mean values as to the true energy values themselves. In other words the rest energy $\frac{1}{2}h\nu$ of the oscillators is not available for interaction with radiation.

Thus leaving aside both the zero-point energy $\frac{1}{2}h\nu$ and the insignificant factor $1/\nu$, as has already been done in (8.6), the mean energy of an oscillator according to quantum theory is

$$\overline{W} = \frac{\sum_{n=0}^{\infty} E_n' e^{-E_n'/kT}}{\sum_{n=0}^{\infty} e^{-E_n'/kT}} = \frac{d \log Z}{d(-1/kT)},$$

$$Z = \sum_{n=0}^{\infty} e^{-E_n'/kT} = \sum_{n=0}^{\infty} e^{-nh\nu/kT} = \frac{1}{1 - e^{-h\nu/kT}}. \tag{6.13}$$

Differentiating $\log Z$, we get the important expression

$$\overline{W} = \frac{h\nu}{e^{h\nu/kT} - 1}, \tag{6.14}$$

which, when inserted in (5.11), yields Planck's radiation law.

Problems

1. A piece of solid matter consists of N atoms which may be imagined to be three-dimensional oscillators with a given frequency ν. What will be the internal energy of the piece of matter due to thermal oscillations of the atoms? Compute its heat capacity. Note that the zero-point energy is insignificant in the problem of heat capacity.
2. From equations (6.1) and (6.6) compute

$$\frac{\partial(t, E)}{\partial(q, p)},$$

and prove that it equals 1.

7. EINSTEIN'S DERIVATION OF PLANCK'S RADIATION LAW

Interaction of Radiation with Real Atoms and Molecules

In 1916 Albert Einstein was able to give a very interesting derivation of Planck's formula based solely upon quantum principles. A characteristic feature of his procedure is that both radiation and matter are treated from the point of view of quantum ideas and that the derivation avoids the use of specific models.

Einstein considers a radiation field representing blackbody radiation which is in thermal equilibrium with a system of atoms and molecules. The properties of these material particles are prescribed only in a very general way. He presupposes that they have definite energy states and that they are able to absorb and emit radiation according to Bohr's frequency law (see Chapter 2, Section 16). Moreover, absorption and emission are governed by statistical laws and determined by some particular probability coefficients.

Consider in particular the transition of an atom or molecule from a state of higher energy E_m to a state with lower energy E_n. The frequency of light emitted in this process or of light absorbed in the opposite process is given by Bohr's frequency law

$$E_m - E_n = h\nu. \tag{7.1}$$

In the general case such states may be composed of several different states having the same energy value. We then have a so-called multiplet with a multiplicity or statistical weight corresponding to the number of coinciding single states. The multiplicities for the upper and lower states are denoted by g_m and g_n, respectively. Let the number of atoms in the two states be N_m and

N_n at thermodynamic equilibrium. According to Boltzmann's law the ratio between these numbers should be

$$\frac{N_n}{N_m} = \frac{g_n e^{-E_n/kT}}{g_m e^{-E_m/kT}}$$

or

$$\frac{g_m N_n}{g_n N_m} = e^{(E_m - E_n)/kT} = e^{h\nu/kT}. \tag{7.2}$$

We now introduce the so-called transition probabilities or Einstein's probability coefficients A_{mn}, B_{mn}, and B_{nm}. (See Fig. 1-5.) They are defined as follows: $g_n A_{mn}$ is the probability (per unit of time) that an atom or a molecule in the state m should make a transition to a lower state n spontaneously, that is, without being influenced from outside. The factor g_n takes account of the fact that the probability increases with the number of coinciding lower states.

We further assume that the probability for a photon of frequency ν to be absorbed and simultaneously to bring an atom from the state n to state m is proportional to the density of radiation $u(\nu)$ of frequency ν. This probability must be proportional to the multiplicity of the upper state, and we put it equal to $g_m B_{nm} u(\nu)$, where B_{nm} is the probability for absorption.

We must now take into consideration the fact that, from a classical point of view, an oscillator in a radiation field may both absorb and emit radiation energy. This depends upon whether by chance the oscillator is accelerated or retarded by the radiation field. Hence we are forced to assume that in the quantum picture there must be a possibility for forced or *induced* emission. The probability for this process, that the system, because of the presence of the radiation field, should be forced to go over from the upper state m to the lower state n and simultaneously emit a photon of energy $h\nu$, must also be proportional to the density of radiation $u(\nu)$ and to the multiplicity g_n of the lower state. We put it equal to $g_n B_{mn} u(\nu)$, where B_{mn} is the probability coefficient of the induced emission.

The condition for thermodynamic equilibrium can now be expressed by stating that the number of quantum transitions from the state m to the state

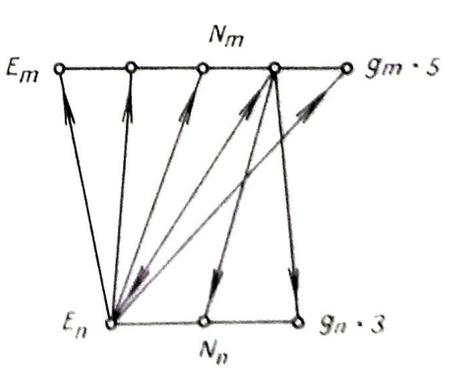

Fig. 1-5. Statistical weight of multiple states.

n must be the same as the number of transitions from n to m. The condition can be expressed in the form

$$N_m g_n (A_{mn} + u(\nu) B_{mn}) = N_n g_m B_{nm} u(\nu). \tag{7.3}$$

Solving the equation with respect to $u(\nu)$ and using (7.2), we obtain

$$u(\nu) = \frac{A_{mn}}{(N_n g_m / N_m g_n) B_{nm} - B_{mn}} = \frac{A_{mn}}{e^{h\nu/kT} B_{nm} - B_{mn}}. \tag{7.4}$$

To obtain Planck's formula we now need only one more postulate, namely, that the above formula must be equivalent to the well-established Rayleigh-Jeans law in the limiting case of $T \to \infty$ or $h \to 0$ for which classical laws are valid. This fixes the coefficient B_{mn}, which must be equal to B_{nm}, and the ratio A_{mn}/B_{nm}. We find

$$B_{mn} = B_{nm}, \qquad \frac{A_{mn}}{B_{nm}} = \frac{8\pi\nu^2}{c^3} h\nu. \tag{7.5}$$

Inserting these values in (7.4), we again have Planck's radiation law.

Probability Coefficients and Wave Mechanics

In wave mechanics, Einstein's probability coefficients or transition probabilities and the corresponding intensities of emission and absorption are expressed by means of so-called matrix elements. More precisely the intensities are proportional to the squares of the absolute values of complex matrix elements. In addition they depend on certain factors also containing the transition frequency $\nu = \nu_{nm}$.

The formula for the absorption coefficient B_{nm} is fairly easy to obtain by means of perturbation calculations. To derive the corresponding formula for A_{mn}, the coefficient of spontaneous emission, more elaborate methods are needed. We can, however, easily guess the true form of the expression by using analogies between the classical and the wave-mechanical treatment of atomic models, particularly that of the harmonic oscillator. The ratio of the probability coefficients as found by this procedure turns out to be the same as in (7.5).

The wave-mechanical formulas for A_{mn} and B_{nm} (as expressed by matrix elements) will be given in later chapters.

8. QUANTUM THEORY OF HEAT. CAPACITY OF SOLIDS

Einstein's Improvement of the Theory of Specific Heat

According to the classical theory of heat an atom or a molecule takes up an amount of heat $\frac{1}{2}kT$ for each translational or rotational degree of freedom.

Hence a single atom has a mean kinetic energy of $\frac{3}{2}kT$, and one mole of a monoatomic gas acquires an intrinsic energy $U = \frac{3}{2}RT$, R being the molar gas constant which approximately equals 2 calories. Hence the specific heat of the gas at constant volume is

$$C_V = \tfrac{3}{2}R = 3 \text{ cal/mole}. \tag{8.1}$$

A diatomic molecule with two rotational degrees of freedom in addition to the three degrees of translational motion has an energy $\frac{5}{2}kT$. Correspondingly, a gas consisting of these molecules has an intrinsic energy $U = \frac{5}{2}RT$ and a specific heat

$$C_V = \tfrac{5}{2}R = 5 \text{ cal/mole}. \tag{8.2}$$

An oscillator, on the other hand, has a mean energy that is equally divided into the potential and the kinetic form. Its total classical mean energy is therefore kT. If an atom of a solid can be fairly well represented by a three-dimensional oscillator making independent and approximately harmonic oscillations in the three main directions of space, we should expect the heat energy of the solid at constant volume to be $3kT$ per atom, and hence the heat capacity to be

$$C_V = N \cdot 3k = 3R = 6 \text{ cal/mole}, \tag{8.3}$$

N being Avogadro's number. For a solid consisting of n-atomic molecules the heat capacity will be

$$C_V = 3nR = 6n \text{ cal/mole}. \tag{8.4}$$

This law of heat capacity of solids as expressed in (8.3) and (8.4) was first set up by Dulong (1785–1838) and Petit (1791–1820) on the basis of experimental evidences. For ordinary substances it is approximately correct at moderate temperatures. Pronounced deviations are found, however, particularly for hard and light substances such as diamond, boron, and silicon. At low temperatures the law ceases to be valid for all substances. The specific heat decreases at low temperatures and tends to zero at $T = 0$.

A general improvement of the Dulong-Petit law was given by Einstein. He replaced the classical mean energy of an oscillator by the corresponding expression as given by quantum theory. For a monoatomic substance, supposing that all atoms have a common characteristic vibration frequency ν, the intrinsic energy becomes

$$U = 3N\left(\frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/kT} - 1}\right) = 3R\left(\frac{\Theta}{2} + \frac{\Theta}{e^{\Theta/T} - 1}\right), \qquad \Theta = \frac{h\nu}{k}. \tag{8.5}$$

In this form of the theory the heat capacity of a substance is characterized by a single parameter, a characteristic temperature Θ which is intimately connected with the hypothetic frequency ν. The specific heat at constant volume

becomes

$$C_V = \frac{dU}{dT} = 3R \frac{(\Theta/T)^2 e^{-\Theta/T}}{(1 - e^{-\Theta/T})^2}. \tag{8.6}$$

At very high temperatures, when $T \to \infty$, the limiting value is $C_V = 3R$ for all substances. At low temperatures the deviation from this value is appreciable. In particular, as $T \to 0$, C_V tends toward zero as $e^{-\Theta/T}$, since the factor $e^{-\Theta/T}$ dominates over the factor T^{-2}.

Debye's Theory of Specific Heat

Although Einstein's theory roughly explains the main deviations of the specific heat of solids from the Dulong-Petit law, it suffers from pronounced insufficiencies in the region of very low temperatures. The reason for this imperfection is easily understood. The atoms or molecules in the space lattice of a solid do not vibrate independently with one and the same or even some few characteristic frequencies. On account of interaction forces between the atoms, the oscillations are coupled. For such complex mechanical systems it is often convenient to resolve the motion of the whole system into some kind of normal vibration. These coupled oscillations may have very different eigenfrequencies, ranging from the very low frequencies of ordinary mechanical and acoustical vibrations to those corresponding to infrared heat radiation. To borrow an appropriate name from optics we have to consider a whole "spectrum" of eigenfrequencies.

In studying the general features of these frequency spectra of solids P. Debye succeeded in improving Einstein's theory considerably. To obtain a preliminary view of the distribution of frequencies consider progressive plane waves of longitudinal or transverse character. From a superposition of such waves we obtain standing waves which we expect to yield a suitable representation of the eigenvibrations of a solid.

If v_l and v_t are the velocities of longitudinal and transverse waves in a solid, respectively, it is possible, as will be shown later (8.25), to calculate the number of eigenvibrations in the frequency range ν to $\nu + d\nu$. For a body of volume V this number may be written as

$$4\pi\nu^2 \, d\nu \, V\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right). \tag{8.7}$$

We here take the velocities to be constants, as in fact they vary very little even up to the highest frequencies. According to the theory of elasticity v_l is larger than v_t but this detail matters very little. Omitting the longitudinal component v_l and putting $v_t = c$ for the transverse waves, we obtain the previous formula for the number of eigenfrequencies in an electromagnetic cavity.

For convenience we now put $v_l = v_t$. If the solid in question consists of N atoms, the mean distance between two neighboring atoms will be approximately

$$d = \left(\frac{V}{N}\right)^{1/3}. \tag{8.8}$$

In contrast to a continuum such a system of material points cannot have infinitely high eigenfrequencies. The frequency spectrum is cut off at a maximum frequency $\nu_{\max}$ and a corresponding minimum wavelength $\lambda_{\min}$. This wavelength must be of the order of magnitude $\lambda = 2d$ corresponding to the oscillations of neighboring atoms with opposite phases.

The frequency spectrum of course depends, although very little, on the shape of the solid body. It is extremely difficult to calculate in detail the distribution. It no longer obeys the simple law (8.7). The number of oscillations decreases more or less irregularly as $\nu \to \nu_{\max}$. It is customary therefore to simplify the problem by accepting the law (8.7) up to some artificial $\nu_{\max}$, where the spectrum is assumed to be abruptly cut off. If in (8.7) we put $v_l = v_t = v$ and integrate from $\nu = 0$ to $\nu = \nu_{\max}$, we get

$$4\pi\left(\frac{\nu_{\max}}{v}\right)^3 V = 3N, \tag{8.9}$$

N being the number of atoms, each of which has three degrees of freedom. Hence

$$\nu_{\max} = v\left(\frac{3}{4\pi}\frac{N}{V}\right)^{1/3}, \qquad \lambda_{\min} = \frac{v}{\nu_{\max}} = 2d\left(\frac{\pi}{6}\right)^{1/3}. \tag{8.10}$$

The specific heat is now obtained by substituting (8.7) with $v_l = v_t = v$ for the number of eigenvibrations in the frequency range $d\nu$ in (8.6) and then summing up the heat capacities for each separate eigenvibration from $\nu = 0$ to $\nu = \nu_{\max}$. Thus we obtain

$$C_V = \int_0^{\nu_{\max}} \frac{4\pi\nu^2 \cdot 3kV}{v^3} \cdot \frac{(h\nu/kT)^2 e^{-h\nu/kT}}{(1 - e^{-h\nu/kT})^2}\, d\nu. \tag{8.11}$$

To express the integral in a more comprehensible form we introduce new variables

$$x = \frac{h\nu}{kT}, \qquad x_0 = \frac{h\nu_{\max}}{kT}, \tag{8.12}$$

and put further

$$\left(\frac{\nu_{\max}}{v}\right)^3 V = \frac{3}{4\pi} N. \tag{8.13}$$

We then obtain

$$C_V = 3R \cdot \frac{3}{x_0^3} \int_0^{x^0} \frac{x^4 e^{-x}}{(1 - e^{-x})^2}\, dx. \tag{8.14}$$

We now introduce the characteristic temperature or the so-called Debye temperature

$$\Theta_D = \frac{h\nu_{\max}}{k} \qquad \text{or} \qquad x_0 = \frac{\Theta_D}{T}. \tag{8.15}$$

For temperatures appreciably higher than Θ_D we have $x_0 \ll 1$. In this case we have approximately

$$C_V = 3R \cdot \frac{3}{x_0^3} \int_0^{x^0} x^2\, dx = 3R, \tag{8.16}$$

which is the classical formula. For intermediate values of x_0, that is, for temperatures near Θ_D, a simple formula cannot be given. However, for very large Θ_D or for very small T, $x_0 \to \infty$ and the upper limit of the integral (8.16) can be replaced by ∞. Making use of the known integral

$$\int_0^\infty \frac{3x^4 e^{-x}}{(1-e^{-x})^2}\, dx = 72\left(\frac{1}{1^4} + \frac{1}{2^4} + \cdots\right) = 72 \cdot \frac{\pi^4}{90}, \tag{8.17}$$

we obtain

$$C_V = 3R \cdot \frac{4}{5}\pi^4 \cdot \frac{T^3}{\Theta_D^3}. \tag{8.18}$$

Hence we see that in this case also the specific heat decreases very rapidly as $T \to 0$ but nevertheless much more slowly than in Einstein's theory, namely, according to the law T^3 instead of $e^{-\theta/T}$. In this region the rate of decrease as given by formula (8.18) has been verified very accurately by measurements of specific heat for a great number of substances.

Table 1-1. $C_V/3R$ **According to Debye's and Einstein's Theories.**

$x_0 = \theta_D/T$	Debye	Einstein
1	0.952	0.954
2	0.826	0.832
4	0.503	0.496
6	0.266	0.230
8	0.138	0.090
10	0.076	0.033
12	0.045	0.010
14	0.0284	0.0030
16	0.0190	0.0009
18	0.0134	0.00025
20	0.0098	0.00007

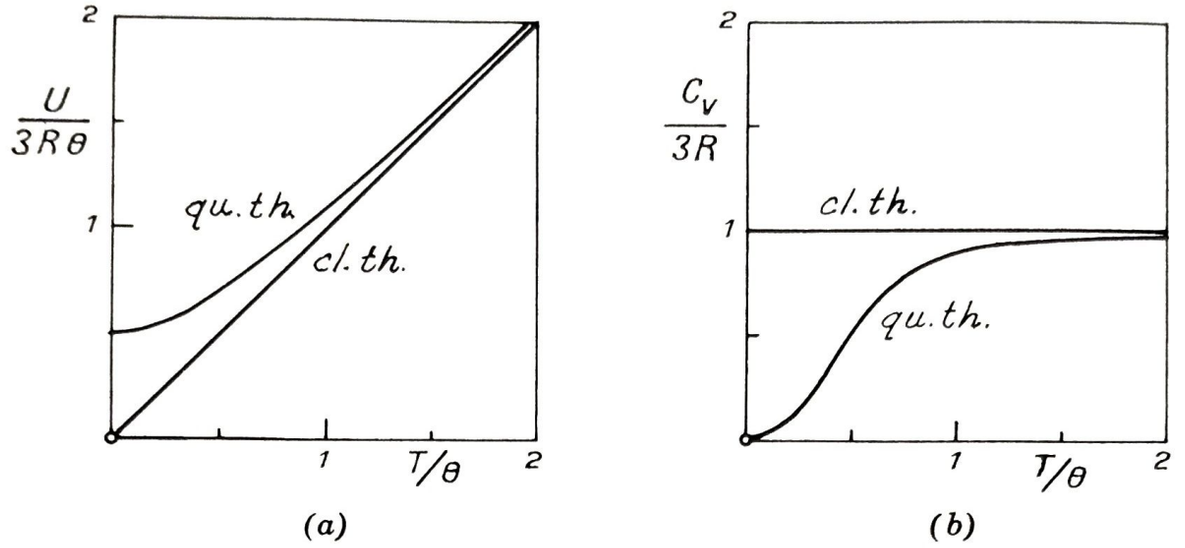

Fig. 1-6. (*a*) Intrinsic energy of a solid according to classical and quantum theories. (*b*) Specific heat according to classical theory and Einstein's theory.

In Table 1-1, Θ and the common eigenfrequency ν_E in Einstein's theory have been adjusted to the Debye temperature Θ_D (and hence to the maximum frequency $\nu_{\max}$) in such a way that the specific heat will be approximately the same above the temperature Θ_D. We have put $\nu_E = \frac{3}{4}\nu_{\max}$, $\Theta_E = \frac{3}{4}\Theta_D$. Also according to Debye's theory the specific heat decreases rapidly at low temperatures, and at $T = \frac{1}{20}\Theta_D$ it amounts to only 1 percent of its asymptotic value $3R$. According to Einstein's theory, however, the specific heat is less than a hundredth of the value given by Debye's theory. Because of the importance of the low temperature region Debye's theory of specific heat is an essential improvement over Einstein's theory. See Figs. 1-6*a* and 1-6*b*.

Calculation of Eigenfrequency Distribution in Solids

We repeatedly have had need for knowing the number of eigenvibrations within a given frequency range for continua (the electromagnetic field in a cavity) as well as for matter consisting of atoms. It will therefore be useful to investigate this problem in some detail. An exact theory for the eigenvibrations of solids is obtainable only on the basis of crystal lattice dynamics. As the interaction forces between the atoms are more or less unknown we are forced, however, even in this theory, to base the calculation upon incomplete experimental data such as the coefficients of elasticity and the propagation velocity of waves. An important point in this connection is the fact that, both for longitudinal and for transverse waves, the propagation velocity varies only moderately up to fairly high frequencies.

The highest frequencies are not independent of the form of the body, since in this case neighboring atoms are oscillating with opposite phases. Near

the limiting frequency, however, the number of eigenvibrations per frequency interval decreases so much that a knowledge of the accurate distribution is insignificant. We assume therefore that the frequency spectrum of any solid is approximately the same as that for a cube of the same size.

Let a be the length of one side of such a cube. Then

$$\Phi = \cos 2\pi\nu t \sin \pi \frac{lx}{a} \sin \pi \frac{my}{a} \sin \pi \frac{nz}{a} \tag{8.19}$$

is a solution of the equation representing a standing wave. It can be obtained by superposition of sinusoidal progressive waves of the form

$$\sin 2\pi\nu\left(t \pm \frac{lx \pm my \pm nz}{v}\right).$$

As in (3.5), l, m, and n are positive integers and

$$\frac{2\nu a}{v} = L, \qquad L = (l^2 + m^2 + n^2)^{1/2}. \tag{8.20}$$

Superposing in a similar manner corresponding cosine waves, we obtain standing waves of the form

$$\Psi = \cos 2\pi\nu t \cos \pi \frac{lx}{a} \cos \pi \frac{my}{a} \cos \pi \frac{nz}{a}. \tag{8.21}$$

Solutions in which a single cosine is replaced by the corresponding sine will be denoted by Ψ_1, Ψ_2, Ψ_3, for instance,

$$\pi \frac{l}{a} \Psi_1 = -\frac{\partial \Psi}{\partial x}, \qquad \text{etc.} \tag{8.22}$$

The solution Φ is particularly adapted to the boundary condition $\Phi = 0$ for scalar waves at the surface of the cube. For longitudinal vectorial waves we may put

$$\mathbf{u}_l = -\frac{a}{\pi} \nabla\Psi = \mathbf{i}l\Psi_1 + \mathbf{j}m\Psi_2 + \mathbf{k}n\Psi_3, \tag{8.23}$$

since longitudinal waves are irrotational and can be expressed as the gradient of another single wave function. If we use expression (8.23), the normal components of u_1 at the surface of the cube are zero.

Transverse waves, on the other hand, must be expressed by means of a vector potential. As this would necessitate the use of other wave functions than Φ and Ψ we restrict ourselves to the statement that in

$$\begin{aligned} u_{1t} &= \mathbf{j}n\Psi_2 - \mathbf{k}m\Psi_3, \\ u_{2t} &= \mathbf{i}\frac{m^2 + n^2}{l}\Psi_1 - \mathbf{j}m\Psi_2 - \mathbf{k}n\Psi_3 \end{aligned} \tag{8.24}$$

we have two independent solutions for transverse waves with mutually orthogonal directions of polarization.

For any of the waves (8.23) and (8.24) we have the relation

$$\frac{\pi}{2} L^2 \, dL = \frac{4\pi a^3}{v^3} \nu^2 \, d\nu \tag{8.25}$$

which determines the number of eigenfrequencies between ν and $\nu + d\nu$. This leads to expression (8.7) for the total number of longitudinal and transverse waves.

In (8.20), l, m, and n are positive integers whose maximum values are now $L_x = N^{1/3}$. Hence the total number of vibrations for the longitudinal waves and for each polarization type of the transverse waves is

$$L_x^3 = N \tag{8.26}$$

or the volume of a cube having a side of length L_x. In (8.25), however, we have a volume element of this cube between the surface of the spheres L and $L + dL$ in the positive octant of a coordinate system in which the cube may be placed. Therefore (8.25) can be used only as long as $L < L_x$. Between $L = L_x$ and $L = L_x\sqrt{2}$ the surface of the sphere will be cut by the side surfaces of the cube. All that is left of the surface of the sphere between $L = L_x\sqrt{2}$ and $L = L_x\sqrt{3}$ is a spherical triangle whose area decreases as the radius increases. This is illustrated in Fig. 1-7.

To clarify the manner of calculating we shall give a few hints. Let

$$\nu_0 = \frac{vL_x}{2a} \tag{8.27}$$

be the frequency corresponding to $L = L_x$. The maximum frequency is then $\nu_0\sqrt{3}$. Let us write

$$r = \frac{L}{L_x} = \frac{\nu}{\nu_0}. \tag{8.28}$$

Our problem will then be equivalent to the computation of the areas of

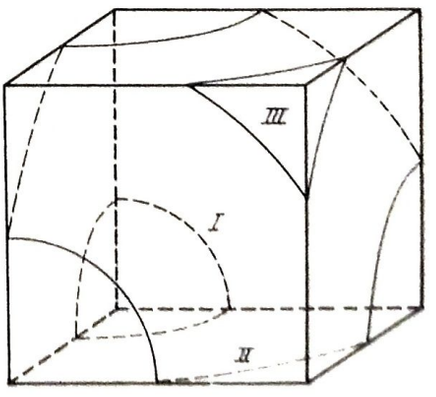

Fig. 1-7. For calculations of the number of eigenvibrations of a cube in a given frequency range. (The cube volume is computed in polar coordinates.)

different parts of a sphere, when the cube in Fig. 1-7 is regarded as a unit cube. The calculations are fairly easy in the two first stages; in the last stage, however, they are rather intricate. Let the area in question, $(\pi/2)r^2\sigma(r)$, be a function of the radius of the sphere. We then have

$$\begin{array}{lll} 0 < r < 1, & 1 < r < \sqrt{2}, & \sqrt{2} < r < \sqrt{3}, \\ \dfrac{\pi}{2} r^2\sigma = \dfrac{\pi}{2} r^2, & \dfrac{\pi}{2}(3r - 2r^2), & \dfrac{\pi}{2}(3r - 2r^2) \\ & & +6r^2 \arctan \sqrt{1 - 2/r^2} \\ & & -6r \arctan \sqrt{r^2 - 2}, \end{array}$$

$$\int \frac{\pi}{2} r^2\sigma \, dr = \frac{\pi}{6}, \qquad \frac{\pi}{12}(13 - 8\sqrt{2}), \qquad 1 - \frac{\pi}{12}(15 - 8\sqrt{2}).$$

Hence

$$\int_0^{\sqrt{3}} \frac{\pi}{2} r^2\sigma \, dr = 1. \tag{8.29}$$

Figure 1-8 shows the number of eigenvibrations of the cube per unit frequency range in the regions $0 < \nu < \nu_0$, $\nu_0 < \nu < \nu_0\sqrt{2}$, $\nu_0\sqrt{2} < \nu_0 < \nu_0\sqrt{3}$, together with the extrapolated curve up to the formal maximum frequency ν_D. The area under the upper curve (extending from $\nu = 0$ to $\nu = \nu_D$) is the same as the area under the full drawn curve, both being equal to N (for all vibrations we should have $3N$).

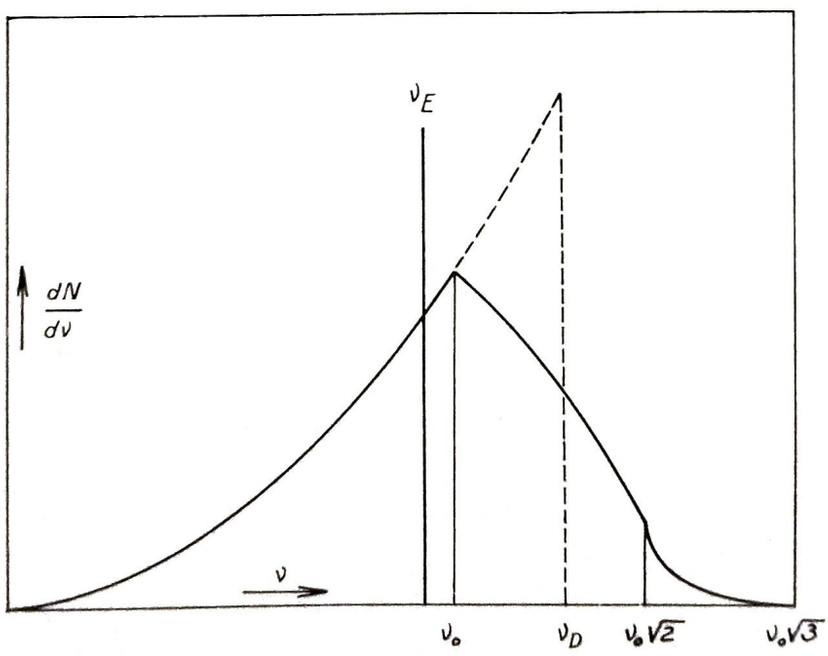

Fig. 1-8. Number of eigenvibrations per frequency interval for a cubical lattice in the simplified Debye theory. The line near to $\nu = \nu_0$ corresponds to the common frequency ν_E of Einstein's theory.

9. THE PHOTOELECTRIC EFFECT

The Photoelectric Law and the Photon Hypothesis

By the photoelectric effect we mean the liberation of electrons from the surface of a metal by impinging light, particularly ultraviolet light and X-rays. The phenomenon was noticed as early as 1888 by Heinrich Hertz (1857–1894) in connection with his famous studies of electromagnetic waves. He observed that spark discharges in the air were influenced by ultraviolet light. In the same year Hallwachs was able to show that light of short wavelength released electrons from a metallic surface. Lenard (1862–1947) studied the phenomenon more closely in vacuum tubes.

The theory of electric conductivity presupposes the existence of free electrons within the metals. From this point of view the phenomenon of photoelectricity itself, that is, a liberation of electrons by the oscillations of the electric field vector, is easily understood. The quantitative aspects of the effect are, however, entirely unintelligible on this basis.

Indeed, as Lenard was able to demonstrate by experiments, the kinetic energy of the liberated electron increases linearly with the frequency of the impinging monochromatic light (this is the *photoelectric law*). The intensity of the light, on the other hand, does not affect the velocity of the ejected electron but manifests itself only in the number of photoelectrons that are produced.

These evidences clearly show that light is essentially different in nature from what we have become accustomed to believe from the study of electromagnetic wave theory. The photoelectric effect can be understood only on the basis of a completely new concept, namely, that light consists of some kind of particles, each of which possesses a certain amount of energy depending on the wavelength of the light. At least from an energy point of view we must think that light can be divided only into given energy quanta of a magnitude depending on the wavelength. These energy quanta we now call *light quanta* or *photons*.

In Planck's first investigation the energy quanta appear as primarily connected with matter: as the smallest amounts of energy that a system of material particles can absorb or release. An inevitable consequence of this idea is that material systems must have discrete energy states that are separated by energy intervals corresponding to the finite energy quanta of radiation. In this way Planck originally conceived how finite quanta of radiative energy could be produced.

Albert Einstein was the first to take the decisive step of applying quantum ideas directly to light. In his famous publication of 1905, *Über einen die Erzeugung und Vernichtung des Lichtes betreffenden heuristischen Gesichtspunkt*, he proposed a kind of corpuscular theory of light. The particles or

energy portions of which light must be considered to consist are just what is now known under the name of photons or light quanta. This concept of light quanta, which after all is an inevitable logical consequence of Planck's energy-level hypothesis for material atomic models, has contributed enormously to the clarity and reliability of our basic physical ideas.

According to Einstein, monochromatic light of a frequency $\nu = c/\lambda$ consists of photons of energy

$$E = h\nu, \tag{9.1}$$

which move rectilinearly away from the light source with the well-known velocity of light. At this stage we shall not try to reconcile the two entirely opposite points of view. From the time of Huygens, Young, and Fresnels, and later in the period of the Maxwell theory and its experimental verification by Hertz, the *wave theory* has been supported by an overwhelming number of reliable experimental facts and logical theoretical deductions. On the other hand, the concept of *light quanta* has been forced upon us by new experimental evidence. For the moment we shall be satisfied to think that, if light appears to spread uniformly out from the light source in the form of spherical surfaces or wave fronts, it is because the photons are numerous. Moreover, if a number of phenomena can be explained only on the basis of the idea of continuous and mutually interfering waves, it is because there must also be some kind of interaction between the photons.

Fluctuation in a Photon Gas

Perhaps we may acquire a better understanding of the frequently discussed duality of light—its wave nature on the one hand, its corpuscular qualities on the other—by studying the so-called *fluctuations* of the radiation. Indeed we have already made use of the fact that radiation in many respects behaves like a gas. The material particles of a gas are also "radiated", in the sense that they have a rectilinear motion with high velocities through space and a corresponding amount of momentum. On the basis of the photon hypothesis the similarity between light and the material atoms or molecules of a gas becomes even more pronounced. It is convenient, therefore, to designate light radiation in general as a photon gas.

Within sufficiently small volumes of an ordinary gas there will be perceptible variations or *fluctuations* both of density and velocity distribution. For instance, the microscopic Brownian motion of dust grains or colloidal particles is caused by such fluctuations. Also light radiation exhibits similar fluctuations. In particular we shall concentrate upon fluctuations of the energy U in a given frequency interval and in a volume element of given magnitude. Fluctuations are defined by the magnitude

$$U - \bar{U} = \bar{\varepsilon}, \tag{9.2}$$

$\bar{U}$ being the mean value of U. Their mean order of magnitude can be measured by the quadratic mean value of the fluctuations. For this quantity we find

$$\overline{\varepsilon^2} = \bar{U}^2 - 2\bar{U}\bar{U} + (\bar{U})^2 = \bar{U}^2 - (\bar{U})^2. \tag{9.3}$$

From

$$\bar{U} = \frac{\int U e^{-U/kT}\, d\tau}{\int e^{-U/kT}\, d\tau}$$

we derive the following important result:

$$\frac{d\bar{U}}{d(-1/kT)} = \frac{\int U^2 e^{-U/kT}\, d\tau}{\int e^{-U/kT}\, d\tau} - \left(\frac{\int U e^{-U/kT}\, d\tau}{\int e^{-U/kT}\, d\tau}\right)^2 = \bar{U}^2 - (\bar{U})^2, \tag{9.4}$$

or

$$\overline{\varepsilon^2} = \frac{d\bar{U}}{d(-1/kT)}. \tag{9.5}$$

This formula we now apply to the radiation energy in a frequency interval from ν to $\nu + d\nu$ and within a limited volume V. We thus obtain

$$\bar{U} = V u(\nu)\, d\nu = V \frac{8\pi\nu^2\, d\nu}{c^3} \cdot \frac{h\nu}{e^{h\nu/kT} - 1}, \tag{9.6}$$

from which follows

$$\frac{\overline{\varepsilon^2}}{\bar{U}} = \frac{d \log \bar{U}}{d(-1/kT)} = \frac{h\nu e^{h\nu/kT}}{e^{h\nu/kT} - 1} = \frac{h\nu}{e^{h\nu/kT} - 1} + h\nu. \tag{9.7}$$

According to (9.6), however,

$$\frac{h\nu}{e^{h\nu/kT} - 1} = \frac{c^3}{8\pi\nu^2} u(\nu), \tag{9.8}$$

and the final result becomes

$$\frac{\overline{\varepsilon^2}}{\bar{U}} = \frac{c^3}{8\pi\nu^2} u(\nu) + h\nu. \tag{9.9}$$

Hence we see that the mean square of fluctuations divided by the mean energy is independent of the volume and the width of the frequency range. The smaller the volume and the frequency range for a given U, the larger are the relative though not the absolute fluctuations. Moreover the mean fluctuation consists of two terms, the last of which tends to zero as $\nu \to 0$. The first term therefore corresponds to the Rayleigh-Jeans law, and hence to the fluctuations given by electromagnetic wave theory. Also, as $h \to 0$ or $\nu \to 0$ the first term in (9.9) tends toward kT, that is, the classical mean energy of an oscillator.

If we apply the same method of calculation to the special Wien radiation law,

$$\bar{U}_W = V u_W(\nu)\, d\nu, \qquad u_W(\nu) = \frac{8\pi\nu^2}{c^3} \cdot h\nu e^{-h\nu/kT}, \tag{9.10}$$

which, as we have seen, is correct in the definitely nonclassical region of large ν's, we find

$$\frac{\varepsilon^2}{\bar{U}_W} = \frac{d \log U_W}{d(-1/kT)} = h\nu, \tag{9.11}$$

that is, the last term of (9.9) which expresses the energy of a single photon.

Equation (9.9), which has been deduced on the basis of the true Planck radiation formula, presents a noteworthy result. It expresses in a particularly clear manner the duality of light, that is, its simultaneous wave and corpuscular nature, and it clearly illustrates the close connection between these two aspects of light.

Magnitude of the Quantum of Action as Obtained from the Photoelectric Effect

As already mentioned photoelectric measurements prove that the energy of photoelectrons increases linearly with the frequency of the impinging light. This is easily explained on the basis of the hypothesis that photons consist of energy quanta $h\nu$. In addition we learn that to release an electron from the interior of the metal a certain amount of work A is required. From the energy principle it then follows that, if e and m are the charge and mass of the electron,

$$\tfrac{1}{2}mv^2 = h\nu - A, \tag{9.12}$$

or

$$h\nu = e(V + V_0), \tag{9.13}$$

if the kinetic energy of the electron and the liberation work are measured in equivalent voltages V and V_0. Then

$$\tfrac{1}{2}mv^2 = eV, \qquad A = eV_0. \tag{9.14}$$

Measuring the energy of the photoelectrons from a given metal for light of various frequencies we find that the results may conveniently be plotted graphically with ν as the abscissa and V in volts as the ordinate. The result will approximately be a straight line as illustrated in Fig. 1-9.

The slope of this line represents the ratio h/e as measured in electrostatic units times a factor of 300 which is the electrostatic unit of voltage as expressed in volts. We thus have

$$\frac{h}{e} = \frac{1}{300}\frac{V}{\nu} = \frac{\lambda V}{300 \cdot c}. \tag{9.15}$$

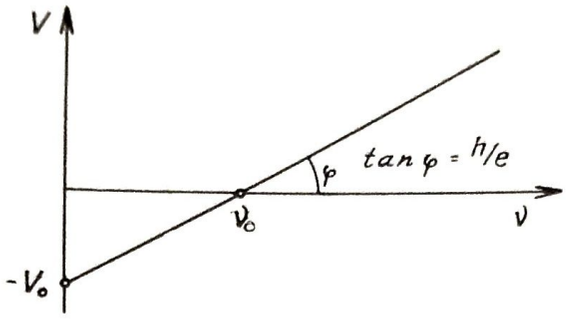

Fig. 1-9. Determination of h/e from the photoelectric effect.

Accurate measurements performed by Millikan in 1916 led to the following figures in the case of lithium and sodium, respectively,

$$\frac{h}{e} = 1.379 \cdot 10^{-17} \qquad \text{and} \qquad \frac{h}{e} = 1.375 \cdot 10^{-17}. \tag{9.16}$$

If combined with the value of the electronic charge as obtained from earlier measurements by Millikan, these figures provide the following approximate values of the quantity of action.

$$h = 4.774 \cdot 1.377 \cdot 10^{-27} = 6.574 \cdot 10^{-27} \text{ erg sec.} \tag{9.17}$$

The more accurate values of $e = 4.8025 \cdot 10^{-10}$ and $h = 6.624 \cdot 10^{-27}$ according to Birge have been referred to earlier.

X-ray production constitutes another important field of application of Einstein's photoelectric law. The work $A = eV_0$ which is required for liberation of electrons from the metal is usually so small in comparison to the energy of X-ray quanta exchanged per photon or per electron that it can often be neglected. If for the production of X-rays we use electrons accelerated by a known voltage V, the electrons will produce bremsstrahlung or "white" radiation, that is, X-rays of all kinds of frequencies below a limiting frequency ν_{max}. This limiting frequency and the equivalent wavelength λ_{min}, which can easily be measured by means of X-ray spectroscopy, correspond to the transition of the whole kinetic energy of an electron into a single photon. This presents another possibility of determining h/e, since

$$h\nu_{max} = eV \qquad \text{or} \qquad \frac{h}{e} = \frac{V\lambda_{min}}{c}. \tag{9.18}$$

In Fig. 1-9 the liberation potential V_0 can in principle be found by continuing the straight line until it cuts the ordinate axis on the negative side. This presupposes that a sufficient number of measurements are available for the determination of the line in its full length. A reliable determination of the limiting frequency ν_0 by which the photoelectrons begin to appear is, however, fairly easily obtained, since a number of points of the line near to the abscissa are experimentally available. If the ratio h/e can be considered well

known, or if it can be found accurately enough from the slope of the line, the liberation potential can be calculated from ν_0 according to (9.13).

The same principle can be applied to an analogous effect: the liberation of electrons from the inner electronic shells of an atom and the resulting excitation of characteristic X-ray spectra connected with these shells. If white X-ray radiation is used for this excitation, the liberation work as expressed in $h\nu$ can be found from measurements of the absorption edge in the continuous X-ray spectrum. The absorption edge is due to the fact that a K electron (or L and M electrons) can be liberated only by light quanta of energy larger than a certain $h\nu_{\min}$. On the other hand, the characteristic X-ray spectra can also be excited by bombardment with electrons that have been accelerated by means of a voltage V higher than a minimum voltage $V_{\min}$. The characteristic X-ray lines will start to rise above the continuous background of bremsstrahlung as soon as the voltage V becomes larger than the minimum voltage $V_{\min}$. If we use several different voltages, it is possible to determine fairly accurately the values of $V_{\min}$. Hence h/e can be found from the equation $eV_{\min} = h\nu_{\min}$.

In Fig. 1-9 this corresponds to the determination of two particularly important points on the straight line, namely, its intersection with both of the main coordinate axes.

10. THE COMPTON EFFECT

Change in Wavelength of Scattered Radiation

We shall now discuss another type of experimental evidence that is just as important as the photoelectric effect in supporting the light quantum hypothesis. This is the *Compton effect* which was discovered in 1932 by A. H. Compton (1892–1962).

By the Compton effect we mean the wavelength change radiation scattered by a material body, in particular X-rays of short wavelength which are scattered by light atoms. To make the effect observable homogeneous X-rays must be used, preferably a characteristic X-ray line of short wavelength. The spectrum of scattered radiation in a given direction may be obtained by means of a known crystal as in X-ray spectroscopy. The radiation then proves to contain two components, one of which is the ordinary scattered radiation with no change in wavelength. The other component appears in the spectrogram as a line that is displaced toward the long-waved side of the spectrum. The displacement increases with the scattering angle ϑ as illustrated in Fig. 1-10. Owing to the final breadth of the spectral lines the two lines are not separately observable below a certain minimum value of the scattering angle.

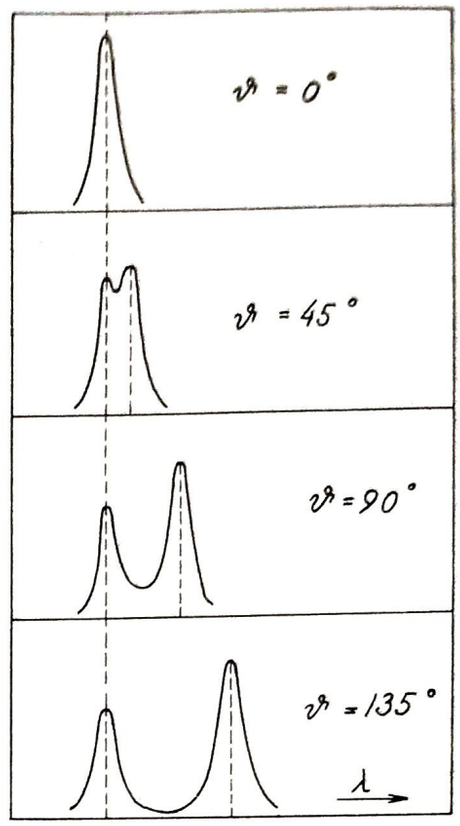

Fig. 1-10. Dependence of the Compton effect on the wavelength.

Interpretation of the Compton Effect as a Collision Process

A theoretical interpretation of this effect was given almost simultaneously by Compton himself and by P. Debye on the basis of Einstein's photon hypothesis. According to this theory the effect is explained as a collision between a photon and an electron which is analogous to an ordinary elastic collision between two macroscopic bodies. In the first approximation the electron is considered to be free. The situation before and immediately after the collision is illustrated in Fig. 1-11.

Initially the photon of energy $h\nu$ is moving toward the free electron. As in a collision between solid spheres, the encounter can take place as a head-on or a noncentral collision. Hence the scattered photon of energy $h\nu'$ can have any direction corresponding to different values of the scattering angle ϑ. Measurements of the wavelength $\lambda' = c/\nu'$ provide values of λ' for different

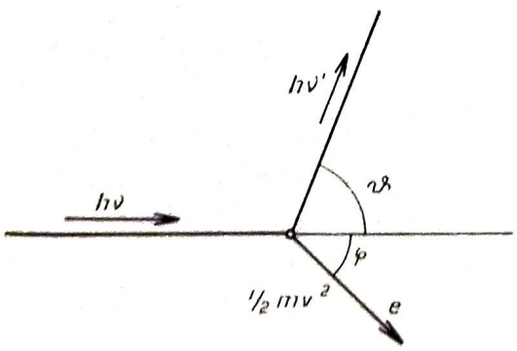

Fig. 1-11. Collision process photon $h\nu$-electron e.

values of the scattering angle ϑ. Usually the direction and the kinetic energy of the electron after the collision cannot be measured. From the laws of conservation of energy and momentum it is possible, however, to establish a sufficient number of equations from which these unknown quantities can be eliminated.

In the Compton effect we are dealing with high energy photons and with corresponding high velocities of the recoil electrons. It is advisable therefore to treat the problem relativistically throughout. It is notable that the relativistic treatment of the Compton effect is in fact the simplest one. The reason for this is mainly that approximate calculations can be avoided.

Let the charge, rest mass, and velocity of an electron be e, m, and v, respectively. The mass of the moving electron is then given by

$$m = \frac{m_0}{(1 - v^2/c^2)^{1/2}}. \tag{10.1}$$

From the energy principle it follows that

$$h\nu - h\nu' = mc^2 - m_0c^2. \tag{10.2}$$

In accordance with electromagnetic theory we assume the momentum of a photon to equal its energy divided by the velocity, that is, $h\nu/c$ and $h\nu'/c$ for the incoming and scattered photon, respectively. The momentum law for two principal directions of the coordinate axes, the one parallel and the other perpendicular to the direction of collision, yields

$$\begin{aligned} \frac{h}{c}(\nu - \nu' \cos\vartheta) &= mv \cos\varphi \\ \frac{h}{c}\nu' \sin\vartheta &= mv \sin\varphi \end{aligned} \tag{10.3}$$

Squaring and adding, we obtain the scalar equation

$$\left(\frac{h}{c}\right)^2(\nu^2 - 2\nu\nu' \cos\vartheta + \nu'^2) = m^2v^2 \tag{10.4}$$

in which the unknown recoil angle φ is eliminated.

From (10.2) we obtain

$$(h\nu - h\nu' + m_0c^2)^2 = m^2c^4,$$

or in connection with (10.1),

$$\left(\frac{h}{c}\right)^2(\nu^2 - 2\nu\nu' + \nu'^2) + 2m_0(h\nu - h\nu') = m^2c^2 - m_0{}^2c^2 = m^2v^2. \tag{10.5}$$

Subtracting (10.4) from (10.5) and dividing by $2m_0h$, we find that the result is

$$\nu - \nu' = \frac{h\nu\nu'}{m_0c^2}(1 - \cos\vartheta). \tag{10.6}$$

Dividing finally by $\nu\nu'/c$, we obtain

$$\Delta\lambda = \lambda' - \lambda = \frac{h}{m_0c}(1 - \cos\vartheta). \tag{10.7}$$

The last equation is the most convenient formula for the Compton effect, as the wavelength difference is expressed in terms of the scattering angle and a single universal constant. The change in wavelength is the same for all kinds of light irrespective of wavelength. Hence it is easily understood why the Compton effect can be observed only for light of extremely short wavelength.

The constant in (10.7) has the dimension of a length (m_0c = momentum, h = momentum × length). It is called the Compton wavelength and may be denoted by λ_C. Its value is

$$\lambda_C = \frac{h}{m_0c} = 0.0242\ A. \tag{10.8}$$

Owing to the relation

$$m_0c^2 = \frac{hc}{\lambda_C} = h\nu_C \tag{10.9}$$

it is theoretically the wavelength of light that would be produced if the total energy of an electron were instantaneously converted into a single light quantum.

As mentioned the Compton scattering is accompanied by an ordinary scattered line with unaltered wavelength. We shall not present the full theory of both lines here but only stress the following facts. In our exposition of the Compton process, we have considered the electron a free electron, since its binding energy (liberation work) is, in general, negligible compared to the energies appearing in (10.2). In a rigorous treatment we should not disregard the liberation work. Next in treating scattering by atomic electrons we must also be aware of the possibility that the electron can remain in the atom. In that event the process has the character of an elastic collision in which the change of the photon momentum is taken up by the whole atom and not by a single recoil electron of comparatively much smaller mass. In this process the energy change is imperceptibly small, hence causing no change in the wavelength of the photon.

11. THE DOPPLER EFFECT

Wavelength Change Caused by Moving Bodies

By the Doppler effect we mean the change in frequency of a wave train of sound or light caused by the relative motion of the observer and the wave center. The phenomenon is easily understood on the basis of wave theory. As the result of the relative motion a larger or smaller number of wave fronts passes the observer in a second than in the case of no relative motion. Hence the Doppler effect can be used to determine relative velocities. More definitely stated, it is the component of relative velocity of the body and the observer in the direction of the connecting line which can be found by measuring the change of frequency. The Doppler effect is of particular importance in astronomy. The enormous distances between the solar system and even the nearest stars of the Milky Way render the determination of relative star velocities by observation of positions extremely difficult. One has to observe for tens or hundreds of years to obtain perceptible changes of relative positions, and even so one merely gets relative velocities perpendicular to the line of vision. In the Doppler effect, however, a physical phenomenon is found which provides a means for instantaneous determination of the unknown component of velocity in the line of vision that would remain unobservable by other means.

In our previous application of the Doppler effect we have been concerned with another aspect of the phenomenon: the change of wavelength in light reflected from a moving body, as for example a piston or, in general, from a moving mirror. In the following we shall keep to this form of the Doppler effect which is directly understandable from the point of view of wave theory.

For this reason we cannot expect to obtain any support for the photon hypothesis from the theory of the Doppler effect. On the other hand, it may be of particular interest to state that it does not exclude the photon concept either. In contrast to interference phenomena, which can be explained exclusively on the basis of wave theory, or the photoelectric and the Compton effect which can be deduced only on the basis of the light quantum hypothesis, the Doppler effect can be understood in either way. We shall not give the usual wave theory derivation of the Doppler effect here; it can be found in elementary textbooks. Instead we shall supplement it with an equivalent quantum theoretical derivation.

Doppler Effect in Light Reflected from Moving Mirrors

To begin with we shall simplify the process of reflection from a moving mirror by disregarding the difference between the angle of incidence ϑ and the angle of reflection ϑ. Moreover we shall be concerned with a mirror

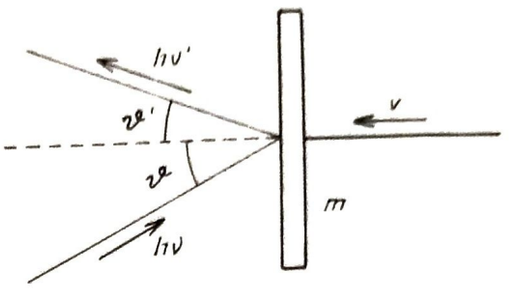

Fig. 1-12. Doppler effect of light reflected from a moving mirror with a normal velocity component v.

moving with a nonrelativistic velocity $v \ll c$. In order to be able to apply the laws of conservation of energy and momentum we must, however, imagine the mirror to have a finite mass m and a velocity v' after a collision with a photon different from v. Subsequently we may pass to ordinary conditions by considering $m \to \infty$ and $v' \to v$, that is, a bound motion of the mirror with constant velocity v. See Fig. 1-12.

Consider a photon with a given frequency and energy ν and $h\nu$ which are changed by reflection into ν' and $h\nu'$, respectively. With the simplification $\vartheta' = \vartheta$ we need only consider the momentum components normal to the face of the mirror. The energy and momentum equations then read

$$\begin{aligned} h(\nu' - \nu) &= \tfrac{1}{2}m(v^2 - v'^2) \\ \frac{h}{c}(\nu' + \nu)\cos\vartheta &= m(v - v'). \end{aligned} \tag{11.1}$$

On dividing, the result is

$$\begin{aligned} \frac{\nu' - \nu}{\nu' + \nu} &= \frac{v + v'}{2c}\cos\vartheta \approx \frac{v}{c}\cos\vartheta \\ \nu' - \nu &\approx 2\nu\frac{v}{c}\cos\vartheta. \end{aligned} \tag{11.2}$$

It should be noted that the characteristic element of quantum concept, the quantum of action h, disappears in our equation by the above treatment. That is the reason for the final result's being the same as in wave theory.

If, on the other hand, we are calculating relativistically, we must allow $\vartheta' - \vartheta \neq 0$ and also take into consideration the components of momentum parallel to the surface of the mirror. As will be shown later we then get two equations for the determination of ν' and ϑ',

$$\begin{aligned} \nu'\left(1 - \frac{v}{c}\cos\vartheta'\right) &= \nu\left(1 + \frac{v}{c}\cos\vartheta\right) \\ \nu'\sin\vartheta' &= \nu\sin\vartheta. \end{aligned} \tag{11.3}$$

These take the place of the former single equation (11.2). As $\nu' > \nu$ it follows

from the latter equation that $\vartheta' < \vartheta$. The difference is small, however, and of relativistic order of magnitude v/c.

Although in the above treatment of the Doppler effect we obtain no support for the quantum hypothesis, we nevertheless must expect a close connection between the Doppler and the Compton effects to exist. This internal connection may have been disguised by some nonessential feature in our description of the reflection process. This is to be found in the assumption of a mirror of infinite mass representing a macroscopic body which automatically precludes any quantum-mechanical effect. We shall therefore consider the whole problem from a wider point of view which allows us to trace the connecting lines between the Doppler and the Compton effects.

Internal Connection between Doppler and Compton Effects

As in the treatment of the Compton effect we again consider a body or a particle of relativistic mass

$$m = \frac{m_0}{(1 - v^2/c^2)^{1/2}} \tag{11.4}$$

and with a momentum $m\mathbf{v}$ which after collision of the body with a photon becomes $m'\mathbf{v}'$. For the present purpose we choose a coordinate system appropriate for each individual collision in taking one of the axes in the direction $m'\mathbf{v}' - m\mathbf{v}$. For a mirror this means that the axis is perpendicular to the reflecting surface; for a smaller body, as for instance an electron, the axis is approximately halfway between the directions of the incoming and the reflected photon.

The velocity directions of the body are designated by the angles φ and φ', those of the photons by ϑ and ϑ', as illustrated in Fig. 1-13. The three equations of (10.2) and (10.3) for the Compton scattering by an electron are now replaced by four: the energy equation

$$\frac{h}{c}(\nu - \nu') + mc = m'c \tag{11.5}$$

and in all three momentum equations (the extra equation resulting from the particular choice of axes)

$$\begin{aligned} \frac{h}{c}(\nu \cos\vartheta + \nu' \cos\vartheta') - mv\cos\varphi &= -m'v'\cos\varphi \\ \frac{h}{c}(\nu \sin\vartheta - \nu' \sin\vartheta') &= 0 \\ mv\sin\varphi &= m'v'\sin\varphi'. \end{aligned} \tag{11.6}$$

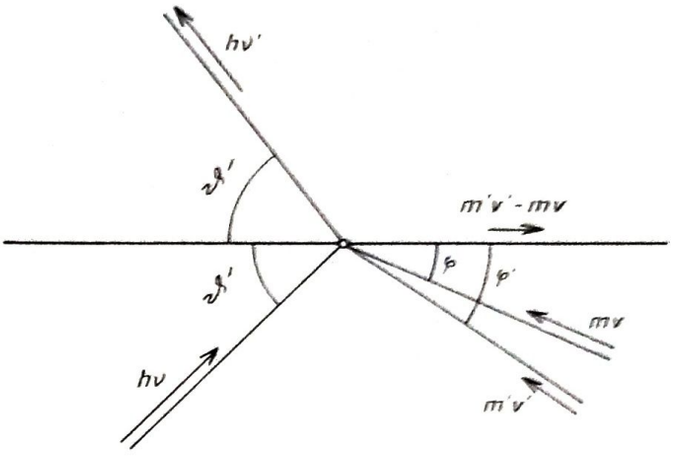

Fig. 1-13. The combined Doppler and Compton effects.

Squaring (11.5) and taking the square sum of (11.6), we obtain the two scalar equations

$$\left(\frac{h}{c}\right)^2(\nu^2 - 2\nu\nu' + \nu'^2) + 2mh(\nu - \nu') + m^2c^2 = m'^2c^2$$

$$\left(\frac{h}{c}\right)^2[\nu^2 + 2\nu\nu' \cos(\vartheta + \vartheta') + \nu'^2] \tag{11.7}$$

$$- 2mh\frac{v}{c}\cos\varphi(\nu\cos\vartheta + \nu'\cos\vartheta') + m^2v^2 = m'^2v'^2.$$

Using (11.4) we get, on subtracting and dividing by $2mh$:

$$\frac{h}{mc^2}\nu\nu'(1 + \cos(\vartheta + \vartheta'))$$

$$= \nu\left(1 + \frac{v}{c}\cos\varphi\cos\vartheta\right) - \nu'\left(1 - \frac{v}{c}\cos\varphi\cos\vartheta'\right). \tag{11.8}$$

For $v = 0$ this is the former equation (10.6) for the Compton effect, the scattering angle of the photon now being $\Theta = \pi - (\vartheta + \vartheta')$. When $v \neq 0$ there is in addition a more or less pronounced Doppler effect. The Compton effect, however, is perceptible only when the mass of the body is very small, of the order of magnitude of an electron mass. In addition the frequency must be large [compare the product $\nu\nu'$ on the left with the difference $\nu - \nu'$ on the right-hand side of (11.8)].

For an appreciably larger mass than the electron mass the left-hand side of (11.8) may be completely neglected. We then get the equations

$$\nu\left(1 + \frac{v}{c}\cos\varphi\cos\vartheta\right) = \nu'\left(1 - \frac{v}{c}\cos\varphi\cos\vartheta'\right) \qquad (11.9)$$

$$\nu\sin\vartheta = \nu'\sin\vartheta'$$

as in (11.3), the difference being merely that v has been replaced by $v\cos\vartheta$. For a mirror this is the component of velocity normal to the surface of the mirror.

CHAPTER 2

The Bohr Atomic Theory

12. THE FOUNDATION OF ATOMIC THEORY AND ITS FIELD OF APPLICATION

The fundamental principles of quantum theory which we have tried to illustrate in the preceding chapter have found their most important and far-reaching application in modern atomic theories. By "atomic theory" we here understand a description of how atoms and molecules are constructed of electrons and unchangeable heavy nuclei with a given mass and electric charge. In this sense atomic theory is substantially a dynamics of the electron. Anything beyond this in the direction of explaining the constitution of the atomic nuclei and the processes going on inside them, whether spontaneous or artificial, belongs rather under the head of nuclear physics. Nuclear physics already embraces vast fields that are still only partially clarified and can therefore not be presented in anything like the form that we can give both classical physics and modern atomic theory, as defined above. Nuclear physics will therefore be excluded from our presentation of atomic theory.

The development of atomic theory took place in two distinct phases, the first in the years after 1913, the second from 1924 to about 1930. Both phases were marked by rapid expansion during their first years. But while the first phase ended in an increasing number of unsolved problems, the second led to a thorough-going clarification of the basic physical concepts. The new atomic physics has become at least as "classical" as the older, so-called classical physics (classical mechanics, including Einstein's theory of relativity and the Maxwell-Lorentz electromagnetic theory).

The first stage in this development and the methods then adopted are closely connected with the model of the hydrogen atom proposed by Niels Bohr in 1913. This is our justification for associating his name with the atomic theory of that period, which will be the subject of our present chapter. The new forms of atomic theory that grew out of the investigations of de Broglie (1892–), Heisenberg (1901–), Schrödinger (1887–1961), Dirac (1902–), and others, are generally referred to either as "quantum mechanics" or "wave mechanics." The latter name fits best with the mode of description here adopted, which will follow in later chapters.

One might be tempted to reduce the description of the Bohr theory to an absolute minimum and even to omit it entirely. For wave mechanics always gives the most reliable results, and we shall necessarily have to familiarize ourselves with its most important features. On the other hand, our thinking is bound to the classical concepts developed from our experiences in the macroscopic world. For most people Bohr's atomic theory, with its semi-classical picture of electron orbits, will therefore still constitute a necessary provisional bridge to the more complex conceptual world which we meet in quantum mechanics. His theory may also offer certain advantages in the purely technical treatment of atomic problems. For instance, the computation of a given definite integral in Bohr's theory, whether exactly or approximately, may at times take the place of the solution of a second-order differential equation in wave mechanics. Such special simplifications have been incorporated into wave mechanics in the form of particular methods of approximation. This indicates that a certain amount of training in the older, Bohr form of atomic theory, far from being a waste of time, may even have a direct practical value.

Series of Atomic Spectral Lines

Owing to the success of spectral analysis in the latter half of the 19th century, in yielding valuable assistance for classification, recognition, and discoveries of chemical elements, the question of a better understanding of spectral lines became, quite naturally, an urgent problem. The discovery of regularities expressible by some simple mathematical law was certainly the first condition for attacking the problem from a true scientific point of view. Progress in that direction was made by the Swiss schoolmaster Balmer (1825–1898) in 1885. He was able to demonstrate a rather peculiar law governing the ratios between wavelengths of different lines in the spectrum from atomic hydrogen. For the most prominent lines H_α ($\lambda = 6563$ Å), H_β ($\lambda = 4861$ Å), H_γ, and so forth, he found the ratios of wavelength to be simple rational fractions. Replacing the wavelength λ by the corresponding frequency ν, we can express the Balmer discovery by the general law

$$\nu = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right), \qquad m = 1, 2, \cdots, \qquad n = m + 1, m + 2 \cdots. \tag{12.1}$$

Dividing by c, we get formally the same law for the wave number per unit length $1/\lambda$, only with a different numerical value of the so-called Rydberg constant R. For the hydrogen atom the wavenumber of the Rydberg constant is

$$R = 109{,}679 \text{ cm}. \tag{12.2}$$

Since $\nu = c/\lambda$ this constant multiplied by the velocity of light $c = 3 \cdot 10^{10}$

cm/sec is the constant R used in (12.1) which will be referred to most frequently later on as the Rydberg constant.

The Balmer series in its proper sense corresponds to the value of $m = 2$. The series comprises the well-known Fraunhofer lines H_α, H_β, H_γ, and H_δ, corresponding to the values of $n = 3, 4, 5, 6$, together with an infinite number of lines from $n = 7$ to $n \to \infty$. As $n \to \infty$ the spectral lines accumulate at a series limit of the wavelength $\lambda = 3646$ Å in the near ultraviolet region of the spectrum. Later on spectroscopists discovered new series, both in the far ultraviolet and in the infrared spectral region. These series are called the Lyman series ($m = 1, n = 2, 3, \cdots$) and the Paschen series ($m = 3, n = 4, 5, \cdots$), respectively. Formula (12.1) gives the wavelength of any lines in the atomic hydrogen spectrum. It is remarkable that every line indicated by the formula exists.

On the basis of later investigations by Rydberg (1854–1919) Ritz, Kayser, and Runge, the possibilities of generalization of the Balmer formula were fully realized. These investigators could demonstrate that ordinary series (arc spectrum) of spectral lines from any atom obey laws similar to that valid for the hydrogen spectrum. The frequencies of the lines obey the formula

$$\nu = R\left\{\frac{1}{[m + \delta(m)]^2} - \frac{1}{[n + \delta'(n)]_2}\right\}. \tag{12.3}$$

In this formula m is a given integer, whereas n takes all integral values from $n = m + 1$ to $n \to \infty$. In certain cases we may also have $n = m$. Also $\delta(m)$ and $\delta'(n)$ are different correction terms tending to given limits as $n \to \infty$ (or $m \to \infty$). In the first approximation constant values of δ and δ' (Rydberg correction) yield a fairly good picture of the frequencies of the spectral lines. Allowing for a slow variation of $\delta'(n)$, as for instance $\delta'(n) = \delta'_0 + \delta'_1 n$ (Rydberg-Ritz correction), we obtain in many cases agreement with observed frequencies within a single series of spectral lines.

Apart from a minor correction, sometimes called the *isotopic effect*, the constant R is the same for all atoms. The isotopic effect is due to the finite mass of the nucleus which also causes the nucleus to move around the center of mass of the whole system. This motion is more pronounced for lighter than for heavier atoms. The constant R in (12.3) is again the Rydberg constant. This constant thus appears as a basic quantity in all atomic spectroscopic formulas and, hence, first of all calls for an explanation by atomic theory.

The first term of expression (12.3) also appears in other spectral series from the same atom. For instance, it may be a member of a series of terms with different values of m. This means that the frequency of any spectral line can be written as a difference of two frequency "terms," which are

members of a "term system" characteristic of the atom. These frequency terms are infinite in number. Nevertheless they may be said to be less numerous than the spectral lines and, hence, to yield a simpler characteristic of an atom than the system of spectral lines. Thus for line frequencies we may write

$$\nu = \nu_m - \nu_n, \tag{12.4}$$

which expresses the so-called Ritz' *combination principle.*

A further generalization of the mathematical description of atomic line spectra is obtained by writing for the magnitude of various spectral terms

$$\nu_n = \frac{Z^2 R}{[n + \delta(n)]^2}, \qquad Z = 1, 2, \cdots, \tag{12.5}$$

Here Z gives the degree of ionization of the atom. Then $Z = 1$ indicates the neutral atom and corresponds to the so-called arc spectrum; $Z = 2$ indicates the singly ionized atom that produces the spark spectrum, and so on. The Rydberg correction $\delta(n)$ is different for different terms, although varying fairly little within a given series of spectral terms. If the electron producing the series of spectral lines were removed from the atom, Z would be the total charge of the resulting atomic ion. Hence, $Z - 1$ is the number of electrons that the atom has already lost as reckoned from its normal neutral state.

For the extremely short-waved characteristic X-ray radiation emitted from an atom (K-series) similar, though not quite so simple, formulas apply. In one of these terms corresponding to an electron in the K-sphere, which is nearest to the nucleus, Z has an empirical value approximately equal to the positive charge of the atomic nucleus as measured in electron charges.

The Electron as a Basic Element in Atoms

Various new discoveries as, for instance, that of positive rays by J. J. Thomson (1856–1940), Wilhelm Wien (1864–1928), and other investigators, soon made it evident that electrons play a predominant role in atomic structure. It became clear that positive atomic ions were produced when one or more electrons were removed from a normally neutral atom. This simple fact of the existence of electrons within an atom made it possible to imagine some process capable of explaining some features of light emission and light absorption in atoms. On the basis of the Lorentz electron theory a more concrete picture of an electron had already been formed. For instance, the mass of the electron simply appeared to result from the inevitable inertia of its electrostatic and electromagnetic field. Even an approximate value of the "radius" of the electron could be obtained, say, according to the law $e^2/r_0 = mc^2$ (e = charge, m = mass, r_0 = radius of the electron, c = velocity of light). This "classical" electron radius $r_0 = e^2/mc^2$ is several thousand times

smaller than the linear dimensions of an atom as obtained from the kinetic theory of gases. This subatomic size fits extremely well with the view that electrons are elementary constituents of the atoms.

Electrons moving in an electric or magnetic field are bent out of their rectilinear path by electromagnetic forces. On this basis the ratio e/m was measured by J. J. Thomson and other investigators in the late nineties. Their results were used by H. A. Lorentz (1853–1928) to explain some recent spectroscopic discoveries made in 1896 by his fellow countryman P. Zeeman (1865–1943). Zeeman was able to show that spectral lines emitted from atoms subject to a very strong magnetic field are split into two or three components, the number depending on the direction of observation. Two of these components are symmetrically placed with respect to the original spectral line, the third one being undisplaced. The magnitude of the displacements is to a high degree of accuracy proportional to the strength of the magnetic field. This is the so-called normal Zeeman effect. H. A. Lorentz explained the phenomenon by the following fairly simple considerations.

Lorentz's Theory of the Zeeman Effect

Suppose that, due to forces which we need not understand in detail, an electron is quasielastically bound to an atom and oscillating with an eigenfrequency ν_0. According to Maxwell's electromagnetic theory this electron is capable of absorbing and emitting light of the same frequency. For the present purpose we accept this view as a satisfactory explanation of the origin of the spectral line. The equation of motion for a single electron with coordinate x as measured from the point of equilibrium is

$$\ddot{x} + (2\pi\nu_0)^2 x = 0, \tag{12.6}$$

provided that the amplitude of vibration is small.

Next consider the case that the atom is placed in a magnetic field $\mathbf{H}$, say, in the direction of the z-axis, $H_x = H_y = 0$, $H_z = H$. Owing to the Lorentz force $(-e/c)\mathbf{v} \times \mathbf{H}$ the equations of motion for the x- and y-coordinates are transformed into

$$\begin{aligned} \ddot{x} + (2\pi\nu_0)^2 x &= -\frac{e}{mc} H\dot{y}, \\ \ddot{y} + (2\pi\nu_0)^2 y &= \frac{e}{mc} H\dot{x}, \end{aligned} \tag{12.7}$$

the third equation for the z-component being unchanged.

We now put

$$x = a \cos 2\pi\nu t, \qquad y = b \sin 2\pi\nu t, \tag{12.8}$$

obtaining linear equations for the amplitudes a and b,

$$\begin{aligned}(\nu_0^2 - \nu^2)a + 2\nu_L\nu b &= 0,\\ 2\nu_L\nu a + (\nu_0^2 - \nu^2)b &= 0,\end{aligned} \tag{12.9}$$

$$\nu_L = \frac{eH}{4\pi mc}, \qquad \omega_L = 2\pi\nu_L = \frac{eH}{2mc},$$

ω_L is usually called the Larmor frequency. The solutions of (12.9) are

$$b = \pm a \quad \text{for} \quad \nu^2 - \nu_0^2 = \pm 2\nu\nu_L \qquad \text{or} \qquad \nu \approx \nu_0 \pm \nu_L. \tag{12.10}$$

According to (12.8) the first solution represents a counterclockwise circular motion with an increased frequency of the electron in the xy-plane. The second solution represents a circular motion in the opposite direction and with a lower frequency. Transforming to new coordinates

$$\begin{aligned}x_1 &= x\cos\omega_L t + y\sin\omega_L t,\\ y_1 &= -x\sin\omega_L t + y\cos\omega_L t,\end{aligned} \tag{12.11}$$

in a system rotating counterclockwise with angular velocity ω_L, that is, with the Larmor frequency, the solution

$$x = a\cos(\omega_0 + \omega_L)t, \qquad y = a\sin(\omega_0 + \omega_L)t, \qquad \omega_0 = 2\pi\nu_0, \tag{12.12}$$

simplifies to

$$x_1 = a\cos\omega_0 t, \qquad y_1 = a\sin\omega_0 t. \tag{12.13}$$

Hence the perturbed motion of the electron simply consists in a "Larmor precession" with angular velocity ω_L of the electron orbit.

According to the electromagnetic theory the electron must now emit light of three different frequencies $\nu = \nu_0$ and $\nu = \nu_0 \pm \nu_L$. The perturbed vibration parallel to the z-axis does not emit radiation in the same direction. Looking in the direction of the magnetic field, we therefore observe only the two components of displaced frequency. These are now necessarily circularly polarized, corresponding to their circular motion. In directions perpendicular to the magnetic field the undisplaced component has its maximum intensity. In that direction all three components are observed and all of them are linearly polarized. The direction of polarization of the displaced lines is perpendicular to that of the undisplaced component parallel to the magnetic field, in accordance with the mechanical vibrations for the electron.

This simple theory of the Zeeman effect provides a true and very detailed picture of some features of the interaction between radiation and matter. It is true that it merely explains how absorption and emission of light are modified in atoms, not how radiation is produced or annihilated. It leaves no

doubt, however, that these processes are intimately connected with the motion of electrons within the atoms.

J. J. Thomson's Atomic Model

During the first period after the discovery of the electron physicists naturally stuck to the conception of an atom as an entity similar to compact bodies of the order of gas-kinetic dimensions. It was believed that atoms consisted of electrons imbedded in an atomic "core" of positive electronic charge of much larger dimensions than a single electron. A more detailed picture of this atomic core was proposed by J. J. Thomson, namely, with the total positive electric charge uniformly distributed inside a sphere. Consider the electron near the center of the sphere. It will then be drawn inwards. The force is due to the total charge lying nearer the center of the sphere than the electron itself, and this charge will increase with the third power of the electronic distance. The force will be equal to that produced by the same charge when placed at the center of the sphere. Hence by the inverse square law e/r^2 for the electric field the net result will be a force proportional to the displacement of the electron from the middle point of the atom, that is, a true quasielastic force. The electron should thus be able to perform vibrations with a well-defined frequency and to emit a spectral line of that frequency.

This is the basic idea of Thomson's theory of the atom. For other reasons, however, it became obsolete rather soon. The main reason for this was that the idea of a compact atomic core was not compatible with the more refined scattering experiments which could already be performed at that time. Scientists were trying to determine the "radius" or "cross section" of an atom by means of the penetrating power of fast electrons in different substances. It was found by Lenard, for instance, that the stopping power of nitrogen atoms with respect to fast electrons near the velocity of light behaved as though their cross section were only one millionth or less than that, which was to be expected on the basis of gas-kinetic observations and calculations. Far from acting as a compact "body," the atomic "core" appeared nearly void of matter.

Rutherford's Discovery of the Atomic Nucleus

A decisive step in the investigation of atomic structure was taken by Rutherford (1871–1937) when he introduced the new and more forceful radioactive alpha particles in his scattering experiments. Owing to the appreciably larger mass of these particles, about seven thousand times that of an electron, they will be very little deflected on their way through an atom by the atomic electrons. An eventual scattering of the alpha particles must therefore mainly be caused by the atomic core.

Observations of the scattering of alpha particles soon indicated a concentration of all heavy matter of the atom inside an extremely small domain at the atomic center. The discovery led to the concept of a central body of minute dimensions, the *atomic nucleus*. This nucleus is the carrier of the total mass of the atom (apart from the comparatively negligible electron masses) and also of the total positive electric charge of the atomic core. Since all atoms are found to be electrically neutral in their normal state, the nuclear charge number must correspond to the total number of removable electrons in the normal state of the atom.

To the first approximation the atomic nucleus could simply be regarded as a material point. The anomalous scattering of a fairly small number of alpha particles nevertheless indicated that the atomic nuclei possess some extension in space. They are, however, exceedingly small of the order of magnitude 10^{-12}–10^{-13} cm as compared with atomic dimensions of about 10^{-8} cm. With respect to the topics connected with the description of electronic systems of atoms, the extension in space of atomic nuclei is irrelevant. In this theory the properties of an atomic nuclei are sufficiently defined by the numerical values of two constants, the mass M of the nucleus (which for an atom of a single isotopic chemical element is equal to the atomic weight divided by Avogadro's number N) and the nuclear charge number Z which is an integer when measured in electron charges.

The more refined measurements of nuclear masses, however, soon revealed the existence of atomic or nuclear *isotopes*. By this we mean that within a sample of atoms as found in nature and belonging to the same chemical element there are atoms of different masses. The measurements could be performed by means of the "mass spectrograph," an instrument invented by Aston (1877–1945) for studies of electrically charged atomic particles moving in a combined electric and magnetic field.

In reality the discovery of isotopes led to a further simplification of our picture of an atom. Expressing the mass numbers of atoms in relative measure (choosing O = 16) atomic weights turn out to be approximately integers. Knowing nothing about isotopes, we should infer, for instance, that the mass number of chlorine atoms would be approximately $35\frac{1}{2}$. In our new picture natural chlorine is simply a mixture of chlorine atoms with mass numbers 35 and 37 in the ratio 3:1, approximately. Owing to the presence of electrons we must distinguish between mass numbers for the atomic nucleus and the whole atom. In mass spectroscopy, when preparing tables of mass numbers we have to decide between the one or the other system. Since electrons are by several powers of ten lighter than atomic nuclei, for our purpose we need not go into detail about these matters. As to corrections for nuclear masses in atomic spectroscopy (the Rydberg constant) we shall mainly have to deal with lighter atoms like hydrogen and helium.

Scattering of Charged Particles. Rutherford's Formula

An important task in early atomic research was to invent reliable methods for the determination of the nuclear charge of an atom. The nuclear charge and the number of electrons in the neutral atom are given by the same integer which is also called atomic number. It is this number that uniquely determines the chemical properties of the atom and hence the chemical element to which it belongs. By means of the atomic number or the nuclear charge all 92 elements of the formerly known natural series of chemical elements can be placed in a definite order from $Z = 1$ to $Z = 92$. This number replaces in a convenient way the earlier atomic weight of a chemical element, which was first used for arranging the elements in the well-known periodic system invented by Lothar Meyer (1830–1895) and D. Mendelejeff (1834–1907). The reliability of this new principle was strikingly demonstrated by Moseley (1889–1915) by comparison of wavelengths of characteristic X-ray from neighboring elements in the periodic system. For instance, the succession order of the elements Co ($Z = 27$) and Ni ($Z = 28$) could unambiguously be established by means of X-ray dates and proved to be the opposite of what had been inferred from their atomic weights (Co = 58.97; Ni = 58.68).

At this introductory stage of our discussions it appears natural first to mention the possibilities for determining nuclear charges on the basis of purely classical experiences and considerations. Possibilities of that kind are primarily offered by scattering experiments with alpha particles or short-waved electromagnetic radiation. Important verifications can also be found on a more modern basis relating to quantum-mechanical inferences, as for instance the theory of X-ray spectra (compare Moseley's investigations).

The scattering of alpha particles in an atom can be satisfactorily described (apart from minor refinements) by the so-called Rutherford scattering formula. To derive this formula in an easy way we shall refer to the well-known fact that in the Kepler problem of astronomy nonclosed orbits are hyperbolas with one of their foci at the attraction center. In the case of repulsive Coulomb forces between alpha particles and atomic nuclei the orbits are exclusively hyperbolas. For convenience we refer to Fig. 2-1 representing a hyperbola with its two asymptotes and its two foci. In this figure the orbit of the alpha particle is placed at the left and the atomic nucleus at the focus at the right. For the sake of generality denote the charge of the alpha particle by $Z'e$, where $Z' = 2$, and the resulting formulas will be valid also for other atomic particles, even for fast electrons of negative charge. Imagine a particle of mass m coming in along one of the asymptotes with velocity v_0 and momentum mv_0. It leaves the atom along the other asymptote and with the same velocity v_0. In the turning point at a distance

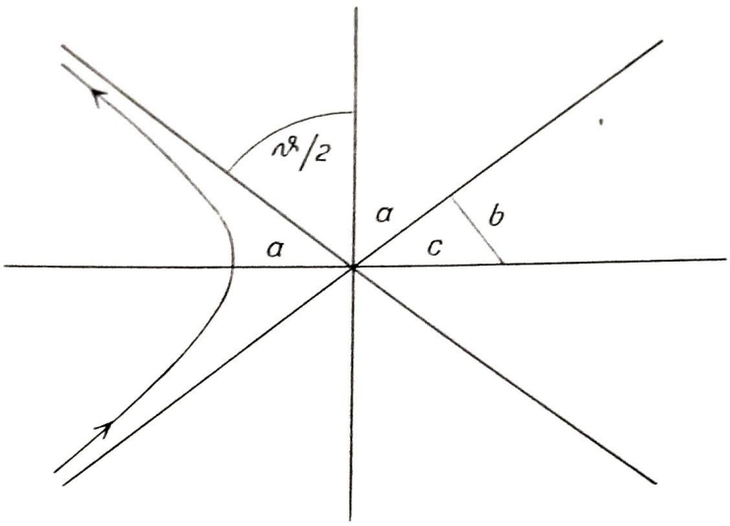

Fig. 2-1. Illustration of the derivation of Rutherford's formula.

$c + a$ from the nucleus it will have a reduced velocity v_1 which we compute as follows.

Denoting the distance of the focus from the asymptote or "impact parameter" by b and half the real axis by a, we have the well-known relations

$$a^2 + b^2 = c^2 \quad \text{or} \quad (c + a)(c - a) = b^2 \qquad b = a \cot \frac{\vartheta}{2}, \tag{12.14}$$

where ϑ is the upper angle between the two asymptotes or the scattering angle. For simplicity the mass of the nucleus is considered infinitely large, even in comparison with that of the alpha particles. The law of linear momentum can then be dispensed with, and we are left only with the energy law and the law of angular momentum. The latter reads

$$mv_0 b = mv_1(c + a). \tag{12.15}$$

Squaring and using (12.14), we obtain

$$v_0^2(c - a) = v_1^2(c + a). \tag{12.15a}$$

Combining the equation with the energy equation

$$\frac{1}{2} mv_0^2 = \frac{1}{2} mv_1^2 = \frac{ZZ'e^2}{c + a}. \tag{12.15b}$$

and eliminating v_1^2, we find that the result is

$$a = \frac{ZZ'e^2}{mv_0^2}, \tag{12.16}$$

or according to (12.14),

$$b = \frac{ZZ'e^2}{mv_0^2} \cot \frac{\vartheta}{2}. \tag{12.17}$$

Consider now a homogeneous beam of particles in the direction of one of the asymptotes as shown in Fig. 2-1. The number of particles with impact parameters between b and $b + db$ and, hence, scattered between the angles ϑ and $\vartheta + d\vartheta$ are

$$N_i 2\pi b\, db = N_s 2\pi \sin\vartheta\, d\vartheta. \tag{12.18}$$

Here N_i is the number of incoming particles per unit time and unit area and N_s is the number of scattered particles per unit time and unit solid angle. The ratio of these two numbers is hence

$$\frac{N_s}{N_i} = \frac{2\pi b\, db}{2\pi \sin\vartheta\, d\vartheta} = \left(\frac{ZZ'e^2}{2mv_0^2}\right)^2 \frac{1}{\sin^4(\vartheta/2)}. \tag{12.19}$$

This is the Rutherford scattering formula.

Scattering of Light. Thomson's Formula

To derive the Thomson scattering formula for electromagnetic radiation we use the acceleration of a free electron in the electric field $\mathbf{E}$ of a light wave,

$$\ddot{\mathbf{r}} = \frac{e}{m}\mathbf{E}. \tag{12.20}$$

From the electromagnetic theory [Part III, Section 22] we find the energy radiated by the accelerated electron per unit time

$$\frac{2e^2}{3c^3}\bar{\ddot{\mathbf{r}}}^2 = \frac{2e^4}{3m^2c^3}\bar{\mathbf{E}}^2. \tag{12.21}$$

From Poynting's theorem the radiant energy passing the unit area in unit time perpendicular to the direction of radiation is

$$S = \frac{c}{4\pi}\bar{\mathbf{E}}^2. \tag{12.22}$$

The fraction of radiation scattered by a single electron is found on dividing (12.21) by (12.22). It is called the total scattering cross section of the electron. If we have N electrons per unit volume, their joint total cross section is

$$\sigma = \frac{8\pi N e^4}{3m^2c^4}. \tag{12.23}$$

This is the Thomson formula for the so-called scattering coefficient per unit volume.

It should be noted that if in (12.23) N is considered a pure number, both (12.19) and (12.23) have the dimension of an area. The true dimension of σ in (12.23) is a reciprocal length.

The quantity (12.23) can be found by measuring the decrease in intensity of a beam of X-rays which passes a layer of atoms. If I_0 is the intensity of the impinging beam and I is the intensity at a depth x of the material, we have

$$\frac{dI}{dx} = -\sigma I \qquad I = I_0 e^{-\sigma x}. \tag{12.24}$$

Measuring I/I_0 for layers of various thickness, we can determine the quantity σ. From σ again, according to (12.23), the number of electrons per unit volume can be found. On the basis of Barkla's measurements of the weakening of X-rays, particularly in lighter materials, the number of electrons per atom could in this way be shown to be $Z = 1$ for H, $Z = 2$ for He, $Z = 3$ for Li, $Z = 6$ for C, and so on.

Problems

1. The wave numbers of the first few spectral lines of the hydrogen atom are

	Lyman Series	Balmer Series	Paschen Series
$1/\lambda =$	82,259.1	15,233.2	5331.5
	97,492.3	20,564.7	7799.3
	102,823.8	23,032.5	9139.8
	105,291.6	24,373.0	9948.1
	106,632.1	25,181.3	10,472.7

Show that the ratios of wave numbers for various pairs of lines are very accurately rational fractions expressible by means of fairly small numbers. Calculate the Rydberg constant R_H for hydrogen.

2. Calculate R_D from the corresponding figures for the heavy hydrogen isotope D (deuterium).

Lyman Series	Balmer Series
82,281.4	15,237.4
97,518.8	20,570.4
102,851.8	23,038.8
105,320.2	24,379.7
106,661.1	25,188.2

3. Calculate R_{He} from the wave numbers of the spectral lines of the positive helium ion

	$m = 1$		$m = 2$
$n = 2$	329,181.2	$n = 3$	60,960.5
3	390,141.7	4	82,296.3
4	411,477.5	5	92,171.6
5	421,352	6	97,536.0

and R_{Li} from the wave numbers of the lines of doubly positive Li

	$m = 1$		$m = 2$
$n = 2$	740,741.9	$n = 3$	137,179.3
3	877,921.2	4	185,190.4

4. For heavy elements the Rydberg constant approaches a limiting value R_∞. The Rydberg constant for any atom is $R_M = R_\infty(1 + m/M)$, m being the electron mass and M the mass of the atom. Evaluate from the various values of the Rydberg constant as obtained from the above calculations the mass ratios of H, D, He, and Li. Can it be seen from the figures which is the predominant isotope of Li 6 and Li 7?
5. The first spectral terms of He as expressed in wave numbers are

	S-Series	*P*-Series	*D*-Series
Para-He:	198,305.0		
	32,033.3	27,175.9	
	13,445.9	12,101.4	12,205.8
	7,370.5	6,818.1	6,864.3
	4,647.2	4,368.2	4,392.5
	3,195.8	3,035.8	3,050.0
Ortho-He:	38,454.7	29,223.4	
	15,073.9	12,746.0	12,209.1
	8,012.5	7,093.6	6,866.2
	4,963.7	4,509.9	4,393.5
	3,374.5	3,117.8	3,050.6

The first spectral terms of the Li S-series are

$$1/\lambda = 43{,}487.2, \quad 16{,}281.1, \quad 8475.1, \quad 5187.7, \quad 3499.6.$$

Use the computed values of R_{He} and R_{Li} and try to find the Rydberg and Ritz corrections for various series. (Note the irregularity of the He ground state due to the lack of the corresponding ortho-state.)

6. The Larmor frequency expressed in wave number is $1/\lambda_L = eH/4\pi mc^2$. Put $\lambda = 5000$, $1\text{Å}/\lambda = 2 \cdot 10^4\ \text{cm}^{-1}$. For what strength of the magnetic field will the Zeeman displacement of the spectral line be 20 cm^{-1} or 5 Å corresponding to $\frac{1}{1000}$ of the wave number of the line? Put $m = 0.91 \cdot 10^{-27}$ g and $c = 3 \cdot 10^{10}$ cm/sec.
7. Formula (12.19) gives the so-called differential scattering cross section of a bare nucleus with respect to alpha particles, that is, the scattering referred to unit solid angle. By multiplying with the surface element of a unit sphere and integrating show that the total scattering cross section is infinitely large.

8. For a single electron the formula (12.23) can be written as $\sigma = (8\pi/3)r_0^2$, where $r_0 = e^2/mc^2$ is the classical or Thomson electron radius. The differential cross section will for unpolarized light be proportional to the Thomson factor $\frac{1}{2}(1 + \cos^2 \vartheta)$. From $\sigma = 2\pi \int_0^\pi \sigma(\vartheta) \sin \vartheta \, d\vartheta$ find the differential cross section $\sigma(\vartheta)$. Try to derive the differential cross section directly from (12.20).

13. ELEMENTARY ATOMIC THEORY

Bohr's Model of the Hydrogen Atom

In 1913 Niels Bohr (1885–1962) created a new situation in atomic research by presenting a new model for the hydrogen atom and a theory for its spectral lines.

His model of the hydrogen atom is very simple. It consists of a hydrogen nucleus, the *proton*, and one electron that moves in a circle around the nucleus. His theory breaks both with Maxwell's theory of electromagnetism and with classical mechanics, that is, with theoretical concepts which at that time were still considered self-evident, although several new viewpoints had appeared as a result of ideas advanced by Planck and Einstein.

Bohr started from two fundamental postulates: (1) Atoms exist in a series of discrete stationary states in which atomic electrons do not radiate electromagnetic energy. (2) Emission of electromagnetic energy from an atom occurs only in connection with a so-called quantum "jump," or quantum transition within the atom. This transition represents an instantaneous change from one stationary state to another and may be described as a jump of an electron from one stationary orbit to another. The energy lost by the atom owing to this change of state is transformed into radiant energy in the form of one single light quantum. Absorption of light is substantially the opposite process.

Postulate 1 abandons electromagnetic laws but makes possible a study of electron orbits of stationary states on the basis of classical mechanics. However, according to Postulate 2 classical mechanics is not valid at the moment when a quantum transition takes place. The theory does not attempt to account for the events from the moment when the initial stationary state ceases to exist until the next stationary state is established. The whole process is as indivisible as the light quantum it produces and like the quantum itself it cannot be analyzed in detail.

Let us examine what can be inferred from the simple case of the hydrogen atom, assuming as already stated that the electron moves in a circle around the nucleus. This motion is one-dimensional with a single position parameter, the arc length of the path or the angle described by the electron vector radius. See Fig. 2-2.

On taking the length of the arc, q, as a coordinate, the velocity v equals $\dot{q}$

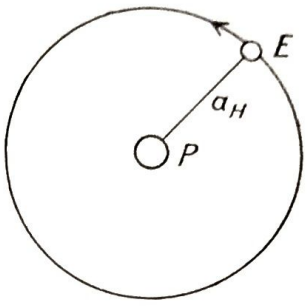

Fig. 2-2. The simplest model of the hydrogen atom, a circular electron orbit.

and the momentum p equals mv. Bohr put the linear momentum of the particle times the length of the circular orbit equal to an integral multiple of the quantum of action, h.

Remembering what has been discussed above, particularly in connection with the harmonic oscillator, we see that this assumption is equivalent to considering q and $p = mv$ as canonically conjugate quantities that may be represented in a two-dimensional phase space.

According to Planck the "cells" of this phase space should always be equal to h. Hence a stationary orbit, as visualized in the phase space diagram, must encompass an area that is given by the phase integral $\oint p\,dq$ along the orbit.

This area we expect to be equal to an integral multiple of h. A constant representing a "zero" phase cell might be added but for our present purpose this constant may be put equal to zero. Hence if a is the radius of the circular electron orbit, the nth stationary state is defined by the equation

$$2\pi amv = nh. \tag{13.1}$$

We now combine this relation with the dynamical equation

$$\frac{mv^2}{a} = \frac{e^2}{a^2} \tag{13.2}$$

which expresses the dynamical equilibrium of the centrifugal force and the nuclear attraction. Finally the total energy of the electron is

$$E = \frac{1}{2}mv^2 - \frac{e^2}{a}. \tag{13.3}$$

From the two first equations we obtain

$$v = \frac{2\pi e^2}{nh}, \qquad a = \frac{e^2}{m}\left(\frac{nh}{2\pi e^2}\right)^2 \tag{13.4}$$

which, when inserted in (13.3), yields

$$E_n = -\frac{Rh}{n^2}, \qquad R = \frac{2\pi^2 e^4 m}{h^3}. \tag{13.5}$$

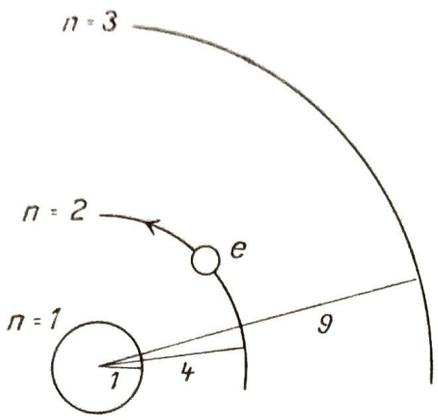

Fig. 2-3. Parts of circular electron orbits in hydrogen corresponding to the first three stationary states.

Thus we have found the energy of the various stationary states of the hydrogen atom and its corresponding electron orbits. The energy is negative with a numerical value that gives the binding energy of the electron. It is proportional to the inverse square of the positive integer n which will be called the *main* (or sometimes the *energy*) *quantum number*. The radius of the orbit is correspondingly proportional to n^2. The possible electron orbits of the atom may therefore be visualized as in Fig. 2-3.

To derive formulas for wavelengths and frequencies of spectral lines emitted by the atom we apply the second postulate. It tells that the energy difference $E_n - E_m$ of the initial and final states n and m by the transition is transformed into a single light quantum. The radiant energy of this quantum is $h\nu$. Hence

$$h\nu = E_n - E_m. \tag{13.6}$$

This is known as the Bohr frequency law. Inserting the energy values as given in (13.5) and dividing by h, we obtain

$$\nu = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right). \tag{13.7}$$

This is exactly the formula (12.1) provided that R in (13.5) can be shown to have the same numerical value as the spectroscopic Rydberg constant. This proves to be true. Hence the most prominent quantity of atomic spectroscopy has been satisfactorily explained on the basis of atomic theory.

The Dependence of the Rydberg Constant on Nuclear Mass

At this stage already we are able to explain such finer details of atomic spectra as the small variations from one atom to another of the Rydberg constant. These variations have been revealed by refined spectroscopic measurements and are of principal importance for the verification of results that can be inferred from atomic theory. They are caused by the finite value of the nuclear mass as compared to that of the electron, which enforces the

nucleus to participate in the movement of the system around the common center of mass of nucleus and electron.

In the case of the hydrogen atom the theory of this effect is very simple and can be generalized immediately to the analogous positive ions He^{+}, Li^{++}, and so forth, containing only one electron. We need only introduce a variable nuclear charge $Z = 1, 2, 3, \cdots$ and a corresponding variable nuclear mass which will be denoted by M. See Fig. 2-4.

To simplify the calculations we first write (13.1) in the form

$$p_\varphi = amv = ma^2\dot{\varphi} = n\frac{h}{2\pi}. \tag{13.8}$$

Here P_φ is the angular momentum which is canonically conjugate to the angle of rotation φ of the line connecting the electron and the nucleus. Equation 13.8 stresses the fact that quantized values of angular momenta are always integral multiples of the constant $h/2\pi$.

In the case of an atomic nucleus of finite mass M moving together with the electron around their common center of mass C (Fig. 2-4), the angular momentum must be expressed in a slightly different way. The distances x and y in the figure will be inversely proportional to m and M, $x:y = M:m$, or

$$x = \frac{M}{M+m}a \qquad y = \frac{m}{M+m} \qquad a = x + y. \tag{13.9}$$

Hence the total angular momentum of the system will be

$$p_\varphi = mx^2\dot{\varphi} + My^2\dot{\varphi} = \frac{mM}{M+m}a^2\dot{\varphi}. \tag{13.10}$$

The dynamical equation (13.2), which might as well have been written $ma^2\dot{\varphi} = e^2/a^2$, is now

$$mx\dot{\varphi}^2 = \frac{mM}{M+m}a\dot{\varphi}^2 = \frac{Ze^2}{a^2}. \tag{13.11}$$

The difference between (13.10) and (13.11) and (13.1) and (13.2) simply consists of replacing the electron mass m by the so-called *reduced mass* of the system,

$$\mu = \frac{mM}{M+m} = \frac{m}{1+m/M} \tag{13.12}$$

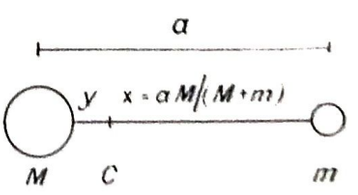

Fig. 2-4. Position of the center of mass C for the electron and the nucleus.

and in addition e^2 by Ze^2. Also the energy equation (13.3) is changed correspondingly into $E = \frac{1}{2}\mu a^2\dot{\varphi}^2 - Ze^2/a$.

In the energy formula (13.5) we therefore simply have to replace the former Rydberg constant—for which we choose the symbol R_∞—by the individual Rydberg constant R_M. In addition, as is easily seen, the energy will be proportional to Z^2. Hence we have

$$E_n = -Z^2 R_M \frac{h}{n^2} \qquad R_M = \frac{R_\infty}{1 + m/M} \tag{13.13}$$

The variation of the Rydberg constant due to mass correction is fairly moderate, even for the lightest atoms. Owing to the extreme accuracy of spectroscopic measurements they are, nevertheless, of great principal and practical importance. The individual Rydberg constants can even be used for computing approximately mass ratios of the lightest nuclei H, D (deuterium), and He. According to Birge their values are

$$\begin{aligned} R_{\mathrm{H}} &= 109{,}677.58\ \mathrm{cm}^{-1} \\ R_{\mathrm{D}} &= 109{,}707.42\ \mathrm{cm}^{-1} \\ R_{\mathrm{He}} &= 109{,}722.26\ \mathrm{cm}^{-1} \\ R_\infty &= 109{,}737.30\ \mathrm{cm}^{-1} \end{aligned} \tag{13.14}$$

Connection between the Classical and Quantum-Theoretic Radiation from an Atom. The Correspondence Principle

The numerical similarities of the results as to the radiation from an atom, according to classical electromagnetism and to quantum theory, is to some degree in contrast to the fundamental difference in the very nature of the radiation processes from the point of view of the two theories. In fact from these numerical similarities we learn that in some way or other there must be an intimate connection between the two theories. It is this fundamental connection that has been expressed in the so-called *correspondence principle.* This principle possesses a considerable formal interest, but it has also been of great practical use in the development of the Bohr form of atomic theory. In some respects it may even be said to have been the pathfinder of the new theories.

The real content of the correspondence principle can be expressed only vaguely. Its meaning is that there will always be a similarity or correspondence between results as obtained from classical laws and those deduced on the basis of quantum theory. A striking example is the linear harmonic oscillator—mathematically the simplest of all atomic models. From the energy values of its stationary states, which will be computed later, we obtain the radiation frequency for transitions between neighboring states

$$\nu = \frac{E_{n+1} - E_n}{h} = \frac{(n + \frac{3}{2})h\nu_0 - (n + \frac{1}{2})h\nu_0}{h} = \nu_0. \tag{13.15}$$

Thus it is the same as the mechanical frequency of the oscillator, and hence also the same as the radiation frequency according to classical electromagnetism. If we anticipate the results of so-called selection rules, that transitions between nonneighboring states are "forbidden," the agreement with respect to radiation frequency is complete. It may also be added that the intensity of radiation is the same as that which would result from classical computations if the oscillator had an intermediate energy $E'_n = \frac{1}{2}(E_n + E_{n+1}) = (n + 1)h\nu_0$.

To compare also the case of hydrogen atom results obtained from the two theories we compute the mechanical frequency of the nth circular orbit. According to (13.4) and (13.8) this is

$$\nu_n = \frac{\dot{\varphi}}{2\pi} = \frac{nh}{4\pi^2 m^2} = \frac{4\pi^2 me^4}{n^3 h^3}$$

or

$$\nu_n = \frac{2R}{n^3}. \tag{13.16}$$

This frequency may be compared with the transition frequency $n \to m$

$$\nu_{nm} = \frac{R}{m^2} - \frac{R}{n^2} = \frac{(n + m)(n - m)R}{n^2 m^2}. \tag{13.17}$$

Considering first only neighboring states $m = n - 1$, we find that the radiation frequency is again very near to the classical frequency of the intermediate state $n - \frac{1}{2}$:

$$\nu_{nn-1} = \frac{(n - \frac{1}{2}) \cdot 2R}{[(n - \frac{1}{2})^2 - \frac{1}{4}]^2} \qquad \nu_{n-1/2} = \frac{2R}{(n - \frac{1}{2})^3}. \tag{13.18}$$

For the hydrogen atom we have a more complex system of selection rules which will be discussed later. According to these rules transitions between nonneighboring states from n to $m = n - 1$, $n - 2$, $n - 3$, and so on, are not prohibited. Hence radiation frequencies occur, which are approximately equal to integral multiples of some mean mechanical frequency, and thus are analogous to overtones in classical acoustics. Nothing similar to such overtones is found in the simple pictures of circular electron orbits. However, by allowing for elliptical orbits of the same quantized energy and applying Fourier analysis to the elliptical motion, the multiple frequency terms or "overtones" automatically appear and increase in strength as the eccentricity of the elliptical orbit increases. Therefore many details concerning electronic motion within the atom, line intensity, polarization rules, and so forth, can be much better understood by frequently consulting the correspondence principle. The exact calculations of transition probabilities and intensities of spectral lines, which have been rendered possible on the basis of wave mechanics, have fully confirmed the approximate validity of the former correspondence principle.

Molecular Models. The Rigid Rotator

In contrast to free atoms, diatomic or polyatomic molecules emit light forming what is called band spectra instead of line spectra. Both atoms and molecules are, however, emitting lines, the difference being mainly that molecular spectra consist of a multitude of individual spectral lines lying close to each other. When these lines are insufficiently resolved they appear as continuous bands or systems of bands. Molecular spectra are therefore frequently termed band spectra. Although only of historical origin the names "line" and "band spectra" are useful alternatives for the names "atomic" and "molecular spectra."

The simplest model of a molecule is the so-called rigid rotator, consisting of two atoms of given mass M_1 and M_2 and at a given internuclear distance R. In this case the potential energy of the two atoms, which is also a constant, can be left out of consideration. Introducing the reduced mass

$$M = \frac{M_1 M_2}{M_1 + M_2} \tag{13.19}$$

as in the case of the hydrogen atom, we may express the angular momentum in the same manner as in (13.8), that is,

$$p_\varphi = MR^2\dot{\varphi} = m\frac{h}{2\pi}, \tag{13.20}$$

where m is an integer $m = 0, 1, 2, \cdots$. The total energy, which is here equal to the kinetic energy, is therefore

$$E_m = \frac{1}{2}MR^2\dot{\varphi}^2 = \frac{1}{2M}\frac{p_\varphi^2}{R^2} = \frac{m^2h^2}{8\pi^2MR^2}. \tag{13.21}$$

The moment of inertia is

$$I = MR^2. \tag{13.22}$$

Hence the total energy can also be written as

$$E_m = \frac{m^2h^2}{8\pi^2I}. \tag{13.23}$$

From the correspondence principle the conclusion can be drawn that the quantum transitions of the rotator are limited to differences $\Delta m = \pm 1$. Applying the Bohr frequency law to the transition $m \to m - 1$, we obtain the optical frequency of the emitted light

$$\nu_{m\,m-1} = \frac{(m - \frac{1}{2})h}{4\pi^2I}. \tag{13.24}$$

On the other hand, we find from (13.20) the mechanical frequency of the rotator

$$\nu = \frac{\dot{\varphi}}{2\pi} = \frac{p_\varphi}{2\pi I}. \tag{13.25}$$

Inserting for p_φ the quantized angular momentum corresponding to a fictitious intermediate state $m - \frac{1}{2}$, we obtain the mechanical frequency

$$\nu_{m-\frac{1}{2}} = \frac{(m - \frac{1}{2})h}{4\pi^2 I} = \nu_{mm-1}. \tag{13.26}$$

This again illustrates the close connection that exists between classical and quantum-theoretical results and which is the main content of the correspondence principle.

The Character of Molecular Spectra

From the correspondence principle it must be concluded that a nonpolar molecule represented by a rigid rotator is unable to radiate light. In order to radiate it must, according to classical electromagnetism, possess an electric dipole moment, for instance, so that the atoms of a diatomic molecule are ionized and oppositely charged.

Molecules of that kind, producing pure rotational band spectra, are comparatively infrequent in nature. Such spectra are also situated far outside the ordinary optical spectral region to the infrared side and hence are rather difficult to observe. The same is true, although to a lesser degree, for the so-called rotation-vibration band spectra. These spectra are caused by transitions between combined vibrational and rotational states of the molecules. Such molecules are not entirely rigid and the atoms of the molecules are vibrating about a mean equilibrium distance in the direction of the molecular axis. The frequencies of the vibrations are considerably higher than the rotational frequencies. Hence, the rotation-vibration band spectra are found much nearer to the visible region of the spectrum than the purely rotational spectra. In this case also the molecules must, according to the correspondence principle, possess an electric dipole moment in order to be able to produce radiation.

The most frequent and best-studied molecular spectra are those produced in connection with electron transitions in the atoms of the molecules. On the relatively high main frequency caused by the electron transition, the smaller vibrational and rotational frequencies are superposed. The bands that result are therefore usually situated in the visible or ultraviolet spectral region. In connection with electron transitions no permanent electric dipole moment of the molecule is needed to produce radiation.

If in the latter case one should try to form an equivalent classical picture of the radiation process, the only thing to do is to replace quite formally the nonclassical electron transition by an oscillating electric dipole of the same frequency as that produced by the electronic transition. On that frequency, as given by the Bohr frequency law for the spectral line which would result if there were no interference with vibrations and rotations of the molecule, the vibrational and rotational frequencies are superposed.

Take that moment to be of the form

$$P_1 = P_0 \sin 2\pi\nu_e t. \tag{13.27}$$

It must be thought of as in some way produced by rapid movements or fluctuations of the atomic electrons (or molecular binding electrons). These electronic fluctuations will depend on the interatomic distance which is suffering a periodic variation with the same frequency ν_v as the much slower vibrations of the molecule. Hence the electric dipole moment will be modified periodically and will contain terms of the form

$$P_2 = P_1 \sin 2\pi\nu_e t \cos 2\pi\nu_v t = \frac{P_0}{2}[\sin 2\pi(\nu_e + \nu_v)t + \sin 2\pi(\nu_e - \nu_v)t]. \tag{13.28}$$

Now suppose the molecule to be rotating about the z-axis with a frequency ν_r. The dipole moment P_2 need not lie in the xy-plane but may form an angle $\vartheta \neq \pi/2$ with the z-axis. The three components of the vector dipole moment will be

$$\begin{aligned} P_x &= P_2 \sin\vartheta \cos 2\pi\nu_r t, \\ P_y &= P_2 \sin\vartheta \sin 2\pi\nu_r t, \\ P_Z &= P_2 \cos\vartheta. \end{aligned} \tag{13.29}$$

We easily see that the two former components can be split up into four terms with different frequencies

$$\nu = \nu_e \pm \nu_v \pm \nu_r, \tag{13.30}$$

whereas the z-component still contains only two,

$$\nu = \nu_e \pm \nu_v. \tag{13.31}$$

According to the correspondence principle this means that, for the rotational quantum number, we have the selection rules $m \to m+1$, $m \to m$, $m \to m-1$. Correspondingly for the vibrational quantum number we should have $n \to n+1$, $n \to n-1$. However, since the molecular vibrations are often rather different from those of a harmonic oscillator, the above selection rules for the vibrational quantum number n are usually broken. The selection rules for m, however, are not influenced by the inner

structure of the molecule. Since the frequencies ν_v and ν_r are much smaller than ν_e, the selection rules apply both to emission and absorption.

The energy of two different states of the molecule can now be written

$$\begin{aligned} E &= E_e + E_v + E_r, \\ E' &= E'_e + E'_v + E'_r. \end{aligned} \tag{13.32}$$

According to the frequency law, $h\nu = E' - E$, a quantum transition between these states produces an optical emission or absorption line of the frequency

$$\nu = \nu_e + \nu_v + \nu_r. \tag{13.33}$$

For each frequency ν_e we may have several oscillational frequencies ν_v, and for each ν_v there will be a great number of rotational frequencies ν_r forming a band. For a given ν_e each individual ν_v corresponds to a band within one and the same band series. Different ν_e yield different series of bands situated in widely different spectral regions.

One problem of theoretical interest is the structure of a single band. In (13.32) we are dealing with two widely different electronic and vibrational states. Accordingly there may be an appreciable difference in the moments of inertia of the two states. Hence if we write

$$\begin{aligned} E_r &= hBm^2 \\ E'_r &= hB'm'^2 \end{aligned} \tag{13.34}$$

there will be a corresponding difference in B and B'.

Because of the selection rules $m' = m + 1$, m and $m - 1$ we obtain from the frequency law three different classes of vibrational frequencies superposed on the frequency $\nu_e + \nu_v$, forming together "branches" of the band,

$$\begin{aligned} \nu_r &= B'(m+1)^2 - Bm^2, \\ \nu_r &= (B' - B)m^2, \\ \nu_r &= B'(m-1)^2 - Bm^2. \end{aligned} \tag{13.35}$$

If these frequencies are illustrated by means of a so-called Fortrat diagram, as a function of m, the succession of frequencies is represented by parts of parabolas as shown in Fig. 2-5 for $B' > B$. Each part gives a so-called branch of the band. In the same order as (13.35) they are called P-, Q-, and R-branches or the positive, zero, and negative branch, according to the selection rules $\Delta m = 1, 0, -1$.

The individual lines of the band are closest to each other near to the combined electron and oscillation transition frequency. This part is called the head of the band. In the above case it has a sharp limit in the negative R-branch to the low frequency side and a slower shading down to the other

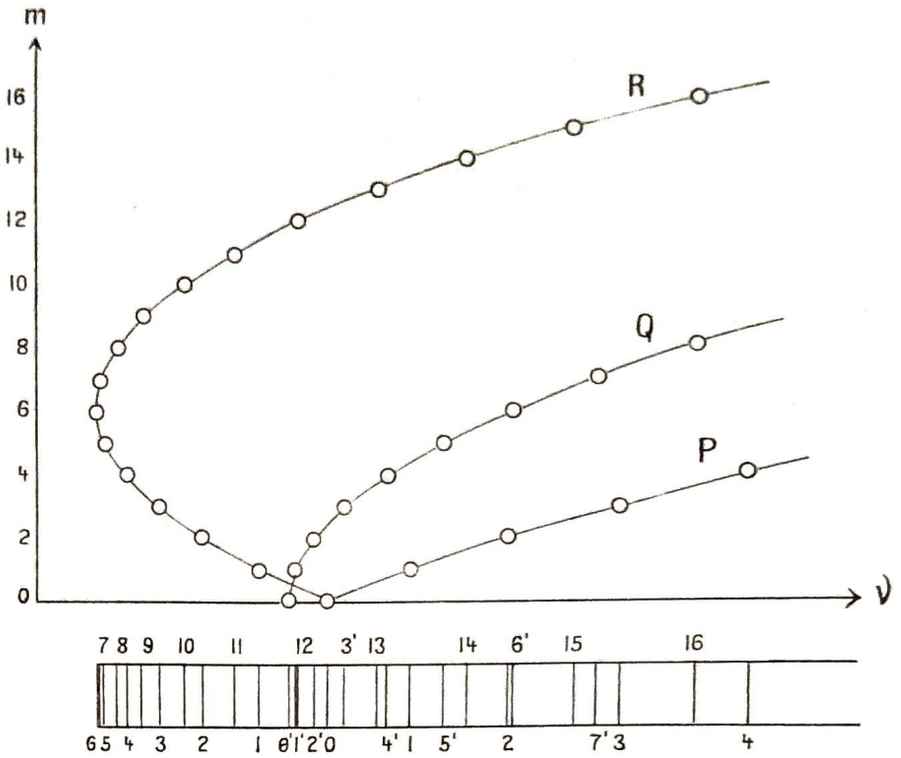

Fig. 2-5. *P*-, *Q*-, and *R*-branches of a band.

side with fewer and fainter lines. The *Q*-branch has a separate and less pronounced head. If $B' < B$, the head of the band is to the high frequency side.

In Fig. 2-6 the potential curves of two different electronic states, together with oscillational energy levels, are illustrated.

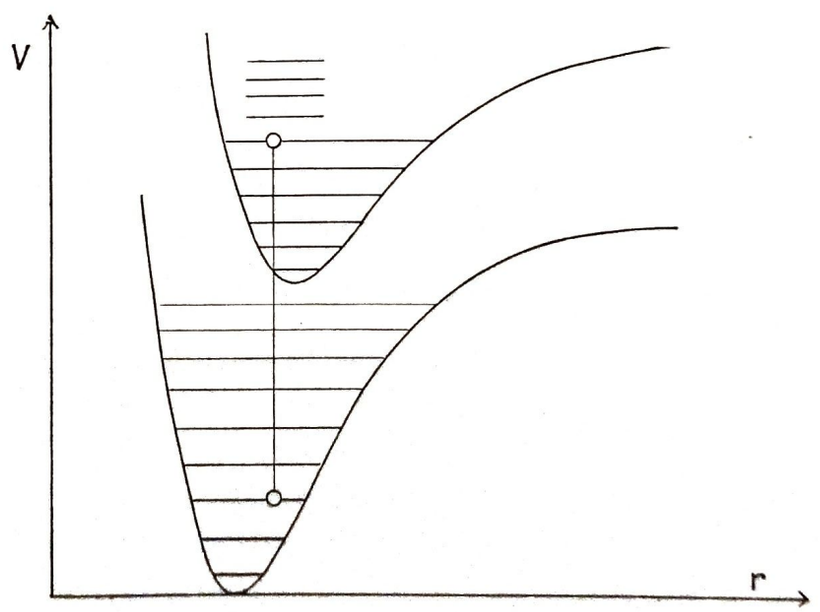

Fig. 2-6. Potential curves of two atoms in a diatomic molecule as a function of their distance. Oscillational states for each electronic state, together with a possible transition between two states, are shown. On the frequency resulting from this transition, rotational frequencies are superposed.

Problems

1. From the values $h = 6.6242 \cdot 10^{-27}$ erg sec, $e = 4.8025 \cdot 10^{-10}$ esu, and $c = 2.99776 \cdot 10^{10}$ cm/sec, in Table 2.1, calculate the reciprocal fine-structure constant $1/\alpha = hc/2\pi e^2$ and prove that it approximately equals 137.030.
2. By means of this value and the value of the Rydberg constant $R_\infty = 109{,}737.30$ calculate the mass of the electron and show that it approximately equals $m = 9.1065 \cdot 10^{-28}$ g.
3. Calculate h/e and compare the result with the values in Section 9 as found by Millikan in 1916.
4. From the values of R_∞ and R_H (13.14) calculate the mass ratio of the proton and the electron and show that it approximately equals 1836.3. What is the mass ratio of the isotope ^1H and the electron?
5. Calculate from R_D and R_{He} the same ratio for the deuteron and the electron, for the alpha particle and the electron, and finally the corresponding ratios of the atomic mass and the electron mass for the two atoms.
6. Calculate the mass of ^1H, ^2H and ^4He. From the atomic weight $^1H = 1.00813$, calculate the Avogadro number and the atomic weights of deuterium and the ordinary helium isotope.
7. Calculate for some reasonable mass M and atomic distance R of a diatomic molecule the rotational spectroscopic constant $h/8\pi^2 I$ and find the spectral region of the pure rotational lines.

Table 2-1. Values of General Physical Constants.

$$
\begin{aligned}
c &= 2.99776 \cdot 10^{10} \text{ cm/sec},\\
N &= 6.02283 \cdot 10^{23}/\text{mole},\\
\frac{e}{c} &= 1.60203 \cdot 10^{20} \text{ emu},\\
e &= 4.80251 \cdot 10^{-10} \text{ esu},\\
h &= 6.6242 \cdot 10^{-27} \text{ erg sec},\\
\frac{h}{e} &= 1.37933 \cdot 10^{-17} \text{ erg sec/esu},\\
m &= 9.10660 \cdot 10^{-28} \text{ g},\\
M_{^1H} &= 1.673393 \cdot 10^{-24} \text{ g},\\
M_{^1H}/m &= 1837.56,\\
^1H &= 1.00813,\\
^2H &= 2.01473,\\
^4He &= 4.00389,
\end{aligned}
$$

Atomic weight of the electron $E = 5.48624 \cdot 10^{-4}$.

From R. T. Birge: *Reports on Progress in Physics*, Vol VIII, 1941. (For error limits compare the original paper.)

14. LAGRANGE'S AND HAMILTON-JACOBI'S MECHANICS IN QUANTUM THEORY

Force and Energy

Using empirical dates concerning atoms and their constituents and relying upon some general quantum laws, we have in the previous section in a rather heuristical way arrived at some usable concepts of atoms and molecules. In this section we shall try to explain the more general principles upon which the older quantum theory was based. First of all, we shall have to deal with some principles of classical dynamics which form one of the main pillars of the theory.

In Part II a detailed presentation of classical mechanics in its more advanced form as given by Lagrange (1730–1813), Hamilton (1805–1865) and Jacobi (1804–1851) will be found. For the sake of convenience some of the main features of this advanced dynamics will be repeated in the present section.

Consider a body (particle, material point) with mass m and Cartesian coordinates x, y, z. The Newtonian equations of motion for the particle are

$$m\ddot{x} = K_x, \qquad \text{etc.} \tag{14.1}$$

We multiply the equations by x, y, z, sum up, and integrate with respect to time from 0 to t. Introducing

$$T = \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \tag{14.2}$$

and denoting by T_0 the same quantity at $t = 0$, we obtain

$$\begin{aligned} T - T_0 &= \int_0^t (K_x\dot{x} + K_y\dot{y} + K_z\dot{z})\, dt \\ &= \int_a^b (K_x\, dx + K_y\, dy + K_z\, dz) = A. \end{aligned} \tag{14.3}$$

The function T is called the *kinetic energy*. Equation 14.3 shows that the increase in kinetic energy is equal to the *work* done by forces acting on the particle during its motion from a to b.

Suppose the force $\mathbf{K}$ to be represented by a space-dependent field of force. An important simplification will then be obtained if the field of force can be expressed as the gradient of a potential V,

$$\mathbf{K} = -\nabla V. \tag{14.4}$$

The integrand then will become a total differential dV and we have

$$T - T_0 = \int_a^b \mathbf{K}\, d\mathbf{r} = -\int_a^b dV = V_0 - V. \tag{14.5}$$

The function V is called the potential energy of the particle. If we write for the last equation

$$T + V = T_0 + V_0 = \text{const} = E, \tag{14.6}$$

the sum of kinetic and potential energy, the total energy E, is a constant. This is one of the simplest forms in which the general principle of conservation of energy can be expressed. The force **K** in (14.4) is therefore called a *conservative* force. Conservative forces are always expressible by means of a potential function. Quite generally it can be stated that forces depending only on mutual distances between interacting particles are conservative forces. If the forces are nonconservative, the integral (14.13), expressing the work done on the particle, will depend on the path of integration between a and b. When the forces are conservative, the integral is independent of the path.

Lagrange's Equations

The Lagrange form of the equations of motion is

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} = 0, \qquad \text{etc.}, \tag{14.7}$$

where

$$L = T - V \tag{14.8}$$

is called the Lagrange function of the coordinates x, y, z, and the velocities $\dot{z}$, $\dot{y}$, $\dot{z}$, or simply the Lagrangian. If we introduce the quantity of motion or momentum **p** of the particle

$$p_x = \frac{\partial L}{\partial \dot{x}} = m\dot{x}, \qquad \text{etc.}, \tag{14.9}$$

we may write instead of (14.7)

$$\dot{p}_x = \frac{\partial L}{\partial x}. \tag{14.10}$$

The particular form of the Lagrange equations of motion are important in coordinate transformations. By introducing any set of general coordinates the form of the equations is preserved. This can most easily be shown by means of the calculus of variations, since the Lagrange equations can be derived from a variational principle. This principle is called the Hamilton principle and is written

$$\int_{t_0}^{t_1} L\, dt = \text{extr.} \tag{14.11}$$

Applying the calculus of variations to this integral, we find that the condition for stationarity of the integral is that the Euler variational derivatives of L

be zero, irrespective of what coordinates have been used. Except for the sign these Euler derivatives are equivalent to the left hand side of (14.7). For one variable the invariant character of the expression (14.7) can easily be shown directly. We put $q = f(x)$, $f(x)$ being an arbitrary function of x. From the equation

$$\dot{x} = \frac{dx}{dq}\,\dot{q} \tag{14.12}$$

we can find the Lagrangian as a function of the general coordinate q and the corresponding "velocity" $\dot{q}$. Equation 14.12 may also be written

$$\dot{q} = \frac{dq}{dx}\,\dot{x}, \tag{14.13}$$

from which we infer

$$\frac{\partial \dot{q}}{\partial x} = \frac{d^2q}{dx^2}\,\dot{x} = \frac{d}{dt}\left(\frac{dq}{dx}\right), \qquad \frac{\partial \dot{q}}{\partial \dot{x}} = \frac{dq}{dx}. \tag{14.14}$$

Combining (14.13) and (14.14), we obtain

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} = \frac{d}{dt}\left(\frac{dq}{dx}\frac{\partial L}{\partial \dot{q}}\right) - \frac{\partial L}{\partial \dot{q}}\frac{\partial \dot{q}}{\partial x} - \frac{\partial L}{\partial q}\frac{\partial q}{\partial x} = \frac{dq}{dx}\left(\frac{d}{dt}\frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q}\right) = 0, \tag{14.15}$$

which is equivalent to the transformed Lagrange equation

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}} - \frac{\partial L}{\partial q} = 0. \tag{14.16}$$

In the case of several variables corresponding transformations can be performed with only modest additional difficulties, as shown in Part II. The general equations are

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0, \qquad i = 1, 2, \cdots, n, \tag{14.17}$$

n being the number of independent coordinates, or the degree of freedom of the system. By means of a double system of variables, the coordinates q_i, together with the momenta p_i, the Lagrange equations can be expressed as a system of simultaneous linear differential equations of the first order,

$$p_i = \frac{\partial L}{\partial \dot{q}_i}, \qquad \dot{p}_i = \frac{\partial L}{\partial q_i}. \tag{14.18}$$

From these equations we obtain a first integral which is identical with the energy integral (14.6),

$$\sum_i p_i \dot{q}_i - L = E. \tag{14.19}$$

This result is easily proved by differentiation with respect to time and by comparison with (14.18).

If, as in the nonrelativistic mechanics of particles, the kinetic energy T is a quadratic function of the velocities, we shall find that

$$\sum_i p_i \dot{q}_i = \sum_i \frac{\partial T}{\partial \dot{q}_i} \dot{q}_i = 2T. \tag{14.20}$$

Hence, with $L = T - V$, (14.19) transforms into $T + V = E$, that is, (14.6).

In relativistic mechanics, and in some other more general cases than that above, we shall have to use a modified Langrangian

$$L = T^* - V. \tag{14.21}$$

Here T^* is no longer the kinetic energy. The latter must be defined by the energy equation. This is equivalent to putting

$$T = \sum_i p_i \dot{q}_i - T^*. \tag{14.22}$$

Relativistic mechanics may be introduced by stating that the mass of a particle depends on the velocity according to the law

$$m = \frac{m_0}{(1 - v^2/c^2)^{1/2}}. \tag{14.23}$$

The functions T^* and T are then found to be

$$T^* = m_0c^2[1 - (1 - v^2/c^2)^{1/2}] \qquad T = m_0c^2\left(\frac{1}{(1 - v^2/c^2)^{1/2}} - 1\right), \tag{14.24}$$

or

$$T^* = -m_0c^2(1 - v^2/c^2)^{1/2} \qquad T = \frac{m_0c^2}{(1 - v^2c^2)^{1/2}}. \tag{14.25}$$

In the latter form the "rest energy" m_0c^2 of the particle has been incorporated in the kinetic energy. The above forms of the auxiliary function T^* are a consequence of the variable relativistic momentum

$$p = mv = \frac{m_0 v}{(1 - v^2/c^2)^{1/2}} = \frac{\partial T^*}{\partial v}, \tag{14.26}$$

which again follows from the variable mass in (14.23).

In the presence of an electromagnetic field

$$\mathbf{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} \qquad \mathbf{H} = \text{curl } \mathbf{A}, \tag{14.27}$$

one must, as shown in Part II, for a particle of charge e, replace T and V in

the Lagrangian $L = T - V$ by

$$T^* = T + \frac{e}{c}(\dot{x}A_x + \dot{y}A_y + \dot{z}A_z) \qquad V^* = V + e\Phi. \tag{14.28}$$

If $T = \frac{1}{2}mv^2$ and $L = T^* - V^*$, this implies that

$$p_x = \frac{\partial T^*}{\partial \dot{x}} = m\dot{x} + \frac{e}{c}A_x \qquad m\dot{x} = p_x - \frac{e}{c}A_x. \tag{14.29}$$

The energy integral, hence, takes the form

$$\begin{aligned} \dot{x}p_x + \dot{y}p_y + \dot{z}p_z - L &= \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + V + e\Phi \\ &= \frac{1}{2m}\left[\left(p_x - \frac{e}{c}A_x\right)^2 + \left(p_y - \frac{e}{c}A_y\right)^2\right. \\ &\quad \left. + \left(p_z - \frac{e}{c}A_z\right)^2\right] + V + e\Phi. \end{aligned} \tag{14.30}$$

Hamilton's Equations of Motion. The Hamiltonian

Suppose the Lagrange equations (14.18) rewritten in a form which expresses $\dot{q}_i$ and $\dot{p}_i$ as functions of q_i and p_i. This system of equations is known under the name of *Hamilton's* or the *canonical equations*. They are most easily expressed by means of the energy function, or the Hamiltonian of the system,

$$H(q_k, p_k) = \sum_i p_i\dot{q}_i - L. \tag{14.31}$$

In the right hand side of this expression the velocities $\dot{q}_i$ are functions of q_i and p_i which can be obtained from the first equation (14.18). Hence the Hamiltonian is a function of coordinates and momenta q_i, and p_i. By (14.18)

$$\sum_i \left(p_i - \frac{\partial L}{\partial \dot{q}_i}\right)\frac{\partial \dot{q}_i}{\partial q_k} = 0, \qquad \sum_i \left(p_i - \frac{\partial L}{\partial \dot{q}_i}\right)\frac{\partial \dot{q}_i}{\partial p_k} = 0.$$

Using these relations we easily find that the Hamilton equations of motion can be expressed as

$$\dot{q}_k = \frac{\partial H}{\partial p_k}, \qquad \dot{p}_k = -\frac{\partial H}{\partial q_k}. \tag{14.32}$$

In the case of conservative forces, or more generally for the time independent Lagrangian and Hamiltonian, that is, $\partial L/\partial t = 0$, $\partial H/\partial t = 0$, we always have

$$\sum_k \left(\frac{\partial H}{\partial q_k}\dot{q}_k + \frac{\partial H}{\partial p_k}\dot{p}_k\right) = \frac{dH}{dt} - \frac{\partial H}{dt} = 0, \qquad H(q_k, p_k) = E, \tag{14.33}$$

E being the constant total energy of the system.

For a single particle in a conservative field of force

$$H = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V. \tag{14.34}$$

If the particle has a charge e and is moving in an additional electromagnetic field, the Hamiltonian, according to (14.30), is changed into

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + (V + e\Phi). \tag{14.35}$$

Thus the electromagnetic field can be accounted for by applying the simple rule of replacing momentum components p_x by $p_x = (e/c)A_x$ and the potential energy V by $V + e\Phi$. If the particle is an electron of charge $(-e)$ and, if by e we mean a positive quantity, we must change the sign of the additional terms.

In relativistic mechanics the equations (14.29) still apply if by m we understand the relativistic mass according to (14.23), thus obtaining

$$\left(\mathbf{p} - \frac{e}{c}\mathbf{A}\right)^2 + m_0^2c^2 = m_0^2c^2 + m^2v^2 = m^2c^2. \tag{14.36}$$

Hence

$$mc^2 = c\{[\mathbf{p} - (e/c)\mathbf{A}]^2 + m_0^2c^2\}^{1/2}, \tag{14.37}$$

and the Hamiltonian is

$$H = mc^2 + V + e\Phi. \tag{14.38}$$

In the absence of an electromagnetic field the relativistic Hamiltonian is

$$H = c(p^2 + m_0^2c^2)^{1/2} + V. \tag{14.39}$$

In the Bohr theory, as well as in wave mechanics the above relativistic or nonrelativistic Hamiltonian is frequently used.

Canonical Transformations

The canonical equations form a system of $2n$ simultaneous differential equations of the first order with $2n$ variables. Equations and variables are doubled in number as compared to the system of n equations of motion of the second order. Consequently the canonical equations are subject to more general transformations than are the ordinary coordinate transformations as mentioned in connection with Lagrange's equations.

By canonical transformations we understand specific transformations in the $2n$ dimensional "phase space" of coordinates and momenta by which the new variables Q_k and P_k satisfy a set of new canonical equations,

$$Q_k = \frac{\partial \bar{H}}{\partial P_k}, \qquad \dot{P}_k = -\frac{\partial \bar{H}}{\partial Q_k}, \tag{14.40}$$

$\bar{H}$ being a function of the new variables Q_k and P_k which is not necessarily equal to the energy of the system.

For simplicity take $\bar{H}$ to be the same as the Hamiltonian H in the variables q_k and p_k. If

$$p_k = \frac{\partial S}{\partial q_k}, \qquad Q_k = \frac{\partial S}{\partial P_k}, \tag{14.41}$$

where $S = S(q_k, P_k)$ is an arbitrary function of the original coordinates q_k and the new momenta P_k and independent of time, then we have

$$\sum_k (p_k \dot{q}_k + Q_k \dot{P}_k) = \frac{dS}{dt}. \tag{14.42}$$

From this relation we easily see that the Hamilton principle can be expressed in different ways, as

$$\begin{aligned} \int_{t_0}^{t_1} L\, dt &= \int_{t_0}^{t_1} \left(\sum_k p_k \dot{q}_k - H \right) dt \\ &= \int_{t_0}^{t_1} \left(-\sum_k Q_k \dot{P}_k - H \right) dt + [S]_{t_0}^{t_1} = \text{extr.} \end{aligned} \tag{14.43}$$

If we consider q_k and P_k to have given values at the terminals t_0 and t_1, variation of the first form of the integral yields the original canonical equation (14.32), whereas the system (14.40) is obtained from the second form. For details we refer to Parts I and II.

Ordinary coordinate transformations are, of course, special forms of canonical transformation. We need not discuss that topic here, since coordinate transformations are best performed at an earlier stage in connection with the Lagrange equations. From these equations, when transformed to the most convenient system of coordinates, we proceed to the Hamilton equations.

Problems

1. A particle of mass m is falling vertically. The acceleration of gravity is g. Denote the height coordinate by z. Find the Lagrangian and the Hamiltonian for the particle. Show that both the Lagrange equations and the canonical equations lead to $\ddot{z} = -g$.
2. Fix the potential energy by putting $V = mgz$. For simplicity write $z = \frac{1}{2}gt^2$. Calculate the integral $\int_0^{t_1} L\, dt$. Next put $z = -\frac{1}{2}gt^2 + ct(t_1 - t)$ and calculate the same integral. Show that it is quadratic in c and has its minimum at $c = 0$.
3. Calculate the integral $\int_0^{t_1} (p\dot{z} - H)\, dt$, $p = \partial L / \partial \dot{z}$ and show that the integral has the same value as the integral in Problem 2. Put $p = -mgt$ and $z = -\frac{1}{2}gt^2 + ct(t_1 - t)$ and show that again the integral is the same as above and has its minimum at $c = 0$.

4. Put $z = -\frac{1}{2}gt^2$ and $p = -mgt + kt$ and show that the integral in Problem 3 is quadratic in k and has its minimum at $k = 0$. Change p into $p = -mgt + f(t)$, where $f(t)$ is an arbitrary function. Prove that the integral has its minimum when the function $f(t)$ vanishes identically.

15. GENERAL INTEGRATION OF CANONICAL EQUATIONS

Hamilton-Jacobi's Differential Equation

To get an idea of how to attack the problem of integrating the Hamilton equations, we shall consider the motion of a particle in ordinary three-dimensional space. At any point in space the potential is given; hence the kinetic energy $T = E - V$ is also a function of coordinates. The magnitude of velocity and linear momentum $\mathbf{v}$ and $\mathbf{p}$ are therefore known quantities but this is not true for the directions of these vectors. Through a given point in space, which can be reached by a particle of total energy E, there may pass an infinite number of possible orbits for the particle.

Consider only one of these orbits and imagine other single orbits going through other points in space. In all of these orbits both magnitude and direction of the linear momentum of the particle will be given. This means that the possible linear momenta of the particle can be expressed by a vector field $\mathbf{p}$. We may then ask if it is possible to choose the orbits of the particle in such a way that the vector field $\mathbf{p}$ can be expressed as a gradient.

$$\mathbf{p} = \nabla S. \tag{15.1}$$

The condition for this is that the "action" function S must satisfy the differential equation

$$\frac{1}{2m}(\nabla S)^2 + V = E, \tag{15.2}$$

which is obtained by substituting (15.1) in the energy equation as expressed by means of the Hamiltonian.

This is a first order partial differential equation of the second degree. In principle it can be solved, and apart from E the solution will contain two integration constants. Consider again (15.1) for a given point in space. It follows that by given E, and hence given magnitude of $\mathbf{p}$ or $\mathbf{v}$, the two additional integration constants permit an arbitrary direction of the velocity of the particle.

If we have an arbitrary number of coordinates, q_i, the obvious generalization of (15.1) is

$$p_k = \frac{\partial S}{\partial q_k}, \tag{15.3}$$

S being a function of all coordinates. Again this representation of possible

momenta is justified if S satisfies the equation

$$H\left(q_k, \frac{\partial S}{\partial q_k}\right) = E. \tag{15.4}$$

This is the *Hamilton-Jacobi differential equation.*

Suppose a solution can be found. If the number of variables is n, the general solution must contain n independent integration constants,

$$S = S(q_k, a_i), \qquad k = 1, \cdots, n, \qquad i = 1, \cdots, n. \tag{15.5}$$

The total energy then can no longer be chosen at will but is a function of the constants a_i,

$$E = E(a_i). \tag{15.6}$$

If wanted, one of the constants, say, a_1 may be expressed by E and the remaining $n - 1$ constants a_i. These constants, together with E, form a complete set of independent integration constants. Let us consider the first alternative of (15.5).

Differentiating (15.4) with respect to one of the constants a_i and using the Hamilton equations, we obtain

$$\frac{\partial E}{\partial a_i} = \sum_k \frac{\partial H}{\partial p_k} \cdot \frac{\partial^2 S}{\partial q_k \, \partial a_i} = \sum_k \dot{q}_k \frac{\partial^2 S}{\partial q_k \, \partial a_i} = \frac{d}{dt} \frac{\partial S}{\partial a_i} \tag{15.7}$$

which, on integrating, becomes

$$\frac{\partial S}{\partial a_i} = \frac{\partial E}{\partial a_i} t + b_i. \tag{15.8}$$

This is a complete solution of the problem. The n equations (15.8) with $2n$ integration constants a_i and b_i, $i = 1, 2, \cdots, n$, provide an implicit representation of the coordinates $q_1, \cdots, q_n$, as functions of time t. The corresponding momenta are given by (15.3).

As a matter of fact, what we did was to perform a special canonical transformation, yielding the canonical equations in a suitable form in which they can easily be integrated. The transformation function which we have used is the function S in (15.5). The integration constants a_i in this function may be taken as new general momenta. They are canonically conjugate to the linear functions of t in (15.8) which will be considered the new general coordinates of the transformation. Denoting them by u_i, we may write

$$u_i = \frac{\partial S}{\partial a_i}. \tag{15.9}$$

Putting

$$\frac{\partial}{\partial a_i} E(a_1, \cdots, a_n) = c_i, \tag{15.10}$$

we get the solution (15.8) in the simple form

$$u_i = c_i t + b_i. \tag{15.11}$$

The term $S(q_k, a_i)$ is called the *action function.*

Cyclic Variables and Constants of the Motion

Suppose the Hamiltonian to be independent of one particular coordinate q_s. From the Hamilton equations it follows that

$$\dot{p}_s = -\frac{\partial H}{\partial q_s} = 0, \qquad p_s = \text{const.} \tag{15.12}$$

In this case q_s is called a cyclic coordinate, and its canonically conjugate momentum p_s is a constant of the motion, that is, independent of time. In the case of conservative fields of force the energy is always a constant of the motion. If a particle is moving in a central field of force, the vectorial angular momentum with respect to the center of force is also a constant of the motion. From the equations

$$\frac{\partial H}{\partial t} = 0, \qquad \frac{\partial H}{\partial \varphi} = 0, \qquad \text{etc.} \tag{15.13}$$

we infer that

$$E = \text{const}, \qquad p_\varphi = \text{const}, \qquad \text{etc.} \tag{15.14}$$

When trying to solve a given atomic problem, whether on the basis of older quantum theory or wave mechanics, it is highly important to find such constants of motion. In simpler problems a complete number of constants, corresponding to the degree of freedom of the system, can sometimes be found, and the integration of the equations of motion is easily performed. In the case of more complex problems, as for instance many electron systems, only an incomplete number of constants of the motion can be picked out easily. These constants are, for instance, the energy, the total angular momentum, and so forth, of the system. No general integration method can therefore be given; one is left with some more or less reliable approximate methods.

The basic idea of introducing Hamilton-Jacobi's differential equations may be stated in this way: If it can be solved, it provides at once a complete system of constants of the motion $a_1, a_2, \cdots, a_n$. The energy function then merely becomes a function of these constants. The corresponding canonically conjugate coordinates will be cyclic variables and linear functions of time as in (15.11). They depend on the original coordinates q_i as expressed in (15.9) by the action function S.

Quasiperiodic Motion. Angle Variable and Action Variables

We must distinguish between the above purely formal integration of the equations of motion for an arbitrary mechanical system and an actual integration for particularly simple systems. The failure of older atomic theory was that it did not succeed in formulating unambiguous quantum rules for other than simple systems. To state it in another way: The theory presupposed a condition that could not be fulfilled, that a complete mechanical description of the system must precede the quantization of the motion.

As a consequence the older theory never reached the state of full generality and true consistency. It was limited to what is known as conditionally periodic or quasiperiodic motion. This kind of motion presupposes that the Hamilton-Jacobi equation can be "separated" in a suitable chosen set of coordinates. Conversely, if a separation is possible, periodic motions can usually be found.

The Hamilton-Jacobi equation is said to be separable if the action function can be written as a sum of single functions, each depending on only one single coordinate,

$$S = S_1(q_1) + \cdots + S_n(q_n) = \sum_k S_k(q_k). \tag{15.15}$$

Hence

$$p_k = \frac{dS_k(q_k)}{dq_k},$$

or in more detail

$$p_k = \frac{d}{dq_k} S_k(q_k, a_i), \qquad i = 1, 2, \cdots, n, \tag{15.16}$$

$a_1, a_2, \cdots, a_n$, being a complete set of constants of the motion. By the form (15.16) we mean that p_k or S_k are functions of the single coordinate q_k but, possibly, depend on all the constants a_i.

Again in quasiperiodic motion we must consider separately two different forms of the motion called *rotation* and *libration*. In the former case P_k is an ordinary periodic function of q_k. For instance, if $q_k = \varphi$ is an angle of rotation, $p_k = p_\varphi$ will be an angular momentum with the period 2π in φ, and rather frequently it may even be a constant. In the case of libration q_k is itself a periodic function of time. This is caused by the particular nature of the function p_k in (15.16) which limits the possible values of the coordinate q_k to a given interval and thus forces q_k to librate between a lower and an upper limit a and b.

Whether or not these quasiperiodic motions are periodic in the ordinary sense depends on the frequencies of the individual rotations and librations. The motion will be periodic if the condition of rationality for the ratios of frequencies is fulfilled. This is why in general the motion of the system is

called conditionally periodic. In applications of quantum rules it is insignificant whether the motion is truly periodic or only quasiperiodic.

In stellar astronomy and even more frequently in quantum theory it has proved suitable to introduce special constants of motion, called *action variables*. They can be defined by phase integrals

$$J_k = \oint p_k(q_k, a_1, \cdots, a_n)\, dq_k, \tag{15.17}$$

taken over a period in the coordinate q_k and thus are functions only of the original constants of the motion a_i introduced in solving the Hamilton-Jacobi equation. Hence

$$J_k = J_k(a_1, \cdots, a_n). \tag{15.18}$$

Conversely we may express a_i by the action variables,

$$a_i = a_i(J_1, \cdots, J_n). \tag{15.19}$$

Hence we may write (15.15) as

$$\begin{aligned} S &= S_1(q_1, J_k) + \cdots + S_n(q_n, J_k) \\ &= \sum_i S_i(q_i, J_k), \qquad k = 1, 2, \cdots, n. \end{aligned} \tag{15.20}$$

The action variables will have canonical conjugates which are called *angle variables* and are denoted by W_k. They are defined by

$$w_k = \frac{\partial S}{\partial J_k}, \tag{15.21}$$

On the other hand,

$$w_k = \nu_k t + b_k, \tag{15.22}$$

where

$$\nu_k = \frac{\partial E}{\partial J_k}. \tag{15.23}$$

It can be proved that an angle variable w_k increases by $\Delta w_k = 1$ for each full period performed by the coordinate q_k. Conversely an increase $\Delta w_k = 1$ of an angle variable ensures that the period has been performed by q_k. According to (15.22) this means that ν_k as defined by (15.23) is the frequency of the periodic motion in q_k.

We now compute the increase of w_k when the system is moved from a position $q_1^{(1)}, \cdots, q_n^{(1)}$, to another position $q_1^{(2)}, \cdots, q_n^{(2)}$, or for brevity, from 1 to 2. Denote the corresponding values of S by $S^{(1)}$ and $S^{(2)}$. Then

$$S^{(2)} - S^{(1)} = \sum_k \int_1^2 p_k(q_k, J_i)\, dq_k \tag{15.24}$$

On the other hand,

$$\Delta w_k = w_k^{(2)} - w_k^{(1)} = \frac{\partial}{\partial J_k}(S^{(2)} - S^{(1)}). \tag{15.25}$$

Since here we are dealing only with coordinate transformations, we need not trouble about the true motion of the system. On integrating (15.24) we may choose an arbitrary variation of the coordinates. If, for instance, the positions 1 and 2 are the same at the end, the initial state of the system is restored. Each individual coordinate q_k will either have been subject to some smaller insignificant oscillations, or it may have performed a certain number of full rotational or librational periods. As a consequence of the definition (15.17) of phase integrals it follows that

$$S^{(2)} - S^{(1)} = \sum_k n_k J_k, \tag{15.26}$$

and hence

$$\Delta w_k = \frac{\partial}{\partial J_k}\left(\sum_i n_i J_i\right) = n_k. \tag{15.27}$$

For a single period of the coordinate q_k

$$\Delta w_k = 1. \tag{15.28}$$

This means that angle variables are particularly well adapted for a Fourier representation of the periodic variations in the coordinates q_k. In general we may write

$$q_k = \sum_{m=-\infty}^{\infty} c_k(m) e^{2\pi i(m_1 w_1 + \cdots + m_i w_i + \cdots m_n w_n)}, \tag{15.29}$$

where both in $c_k(m)$ and in the sum m stands for the whole system of integers $m_1, \cdots, m_i, \cdots, m_n$. A single coordinate q_k will depend not only on the corresponding angle variable w_k but usually also on a number of variables w_i, just as a_i may depend on all J_k. Only in exceptional cases, therefore, can the coordinates be expressed in terms of one-dimensional Fourier series. In general the multiplicity of the Fourier series is the same as the degree of freedom or number of coordinates of the system.

This Fourier representation is of primary importance in subsequent discussions.

16. GENERAL PRINCIPLES IN THE BOHR THEORY

Quantization Rules for Stationary Orbits

Many investigators have contributed considerably to the full development of the older atomic theory. In 1916 Arnold Sommerfeld (1868–1951) announced a complete set of quantum rules for the orbits of a single atomic electron. On these rules he also based his derivation of the famous relativistic

fine structure formula. The same general quantum rules were also proposed by W. Wilson.

In order to discuss more independently the general principles of older atomic theory, we now depart from the historical viewpoint and turn to the more advanced form of the theory to find the shortest possible way to such an insight into the dynamics of electron systems as the theory can afford. Relying in the last resort upon controlling the possibilities offered by wave mechanics, we shall even not hesitate to modify some details of the theory in a reasonable way so as to obtain at once results that modern quantum theory has proved to be true.

As mentioned, the application of general quantum rules is possible only for systems with a separable Hamilton-Jacobi equation. Consider the $2n$-dimensional phase space divided into n two-dimensional phase spaces of pairs of variables q_k and p_k. According to a main principle in quantum theory each two-dimensional phase space must be divided into cells of magnitude h.

Consider a given solution of the equations of motion for a n-dimensional system with constants of motion $a_1, \cdots, a_n$, or $J_1, \cdots, J_n$, the area comprised by the "orbit" in a single phase space will be given by the phase integral

$$J_k = \oint p_k \, dq_k, \tag{16.1}$$

taken over a period of q_k. This area hence is simply equal to the action variable J_k. To be sufficiently cautious we might therefore first propose as a rule that an action variable is changing abruptly by amounts equal to the area h of an elementary cell,

$$\Delta J_k = h. \tag{16.2}$$

It is tempting, as was done during nearly the whole period of older quantum theory, simply to put J_k equal to an integral multiple of h. According to (16.1), however, we may as well take

$$\oint p_k \, dq_k = (n_k + \varepsilon_k)h, \qquad n_k = 0, 1, \cdots, \tag{16.3}$$

leaving the area $\varepsilon_k h$ of the "zero" phase cell for adjustments based upon empirical data.

It may be stated as a useful rule that for rotational motion we have to put $\varepsilon_k = 0$, whereas in the case of librations we have, at least approximately, $\varepsilon_k = \frac{1}{2}$. This may be expressed more briefly by talking of integral and half-quantum numbers for rotation and libration, respectively. For molecular vibrations this leads to the conception of a nonvanishing "zero-point energy" of the ground state of the molecule. The zero-point energy of a harmonic oscillator has proved to be $\frac{1}{2}h\nu_0$ or exactly half an energy quantum.

According to the hypothesis of "material waves" put forward by de Broglie in 1924, a moving particle possesses qualities that can be dealt with only on

the basis of wave concepts. In analogy to photons ($p = h\nu/c = h/\lambda$) the length of these waves must be

$$\lambda = \frac{h}{p} = \frac{h}{[2m(E - V)]^{1/2}}, \tag{16.4}$$

E and V being the total and potential energy of the particle.

For a system with only one degree of freedom it is customary to draw a diagram giving the potential energy as a function of the single coordinate together with the energy levels of the system. Such diagrams are given in Figs. 2-7*a* and 2-7*b*, both for rotational and vibrational motion of a system.

In the case of rotation the condition to thrust upon the "material waves" is necessarily that of periodicity. The period in q must comprise an integral number of waves. Hence by variable wavelength λ as in (16.4) we obtain

$$\oint \frac{dq}{\lambda} = \oint \frac{p}{h}\, dq = n,$$

or, for the phase integral,

$$\oint p\, dq = nh, \qquad n = 0, 1, 2, \cdots. \tag{16.5}$$

In the case of libration we are met with the peculiarity that the "material wave" loses its character of a true wave outside the limiting points for the particle in classical motion. This region is classically prohibited. In wave mechanics the prohibition is not a strict one. To some extent the wave penetrates into the forbidden region, however, by entirely changing its character. The wavelength and the refractive index for the waves become imaginary, and the region outside the classical region behaves as a totally reflecting medium. This means that the wave amplitude decreases rapidly toward zero outside the classical limits.

Utilizing this fact for the benefit of older atomic theory, we may use the following interpretation: The last top of the wave is cut off and the wave is reflected so as to interfere with itself and to form a standing wave. The quantum condition is found by counting the number of waves inside the classical

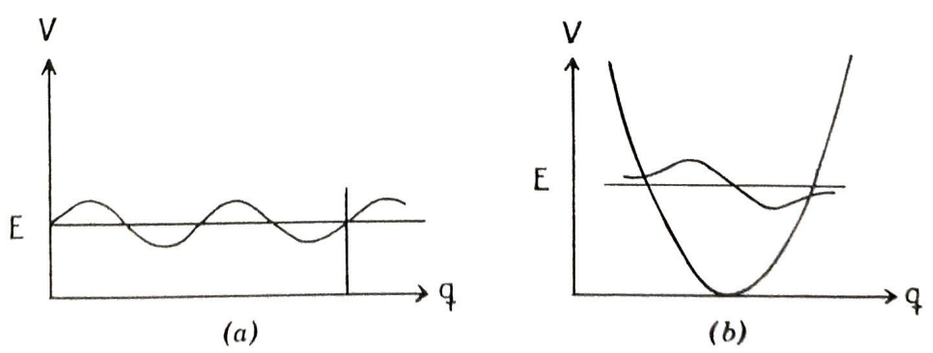

Fig. 2-7. (*a*) Quantization of rotation. (*b*) Quantization of libration.

region, and is given by

$$\oint \frac{dq}{\lambda}.$$

We easily see that the wave is cut off somewhere between the last maximum and the zero point which would have followed in a nonreflecting medium. The wave thereby loses something between zero and a quarter of a wavelength. By wave mechanics it can be shown that the loss is in many cases very near to $\frac{1}{8}$ of a wavelength. For a full period the loss therefore is half a wavelength; the value of the above integral is $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, and so on. The quantum condition for libration hence must be expressed by means of *half* quantum numbers

$$\oint p\,dq = (n + \tfrac{1}{2})h, \qquad n = 0, 1, 2, \cdots. \tag{16.6}$$

The Bohr Frequency Law

According to quantum laws phase integrals and action variables are incapable of assuming continuous values. The mechanical frequencies of classical motion

$$\nu_k = \frac{\partial E}{\partial J_k} \tag{16.7}$$

can therefore no longer be used for expressing optical frequencies. By (15.29) the possible mechanical frequencies, including multiple frequencies or "overtones," are given by the expression

$$\nu = \sum_k m_k \nu_k, \tag{16.8}$$

since $w_k = \nu_k t + b_k$.

We must therefore try to find a plausible generalization of the above equations, and we begin by writing (16.7) in a form as suggested by the definition of derivatives of a function in pure mathematics

$$\nu_k = \lim_{\Delta J_k \to 0} \frac{\Delta E}{\Delta J_k} = \lim_{h \to 0} \frac{E(J_k + h) - E(J_k)}{h}. \tag{16.9}$$

The definition of multiple frequencies or overtones as given by (16.8) can be modified in a similar manner

$$\nu = \lim_{h \to 0} \frac{E(J_1 + m_1 h, \cdots, J_n + m_n h) - E(J_1, \cdots, J_n)}{h}, \tag{16.10}$$

or more briefly written

$$\nu = \lim_{h \to 0} \frac{1}{h} [E_{n_1 + m_1, \cdots n_n + m_n} - E_{n_1 \cdots n_n}], \tag{16.11}$$

We shall now discuss the inevitable consequences that must be drawn from the fact that the universal quantum of action h is finite in magnitude. Since the optical frequency of transition is related to both an upper and a lower state, it can no longer be identified with the mechanical frequencies of either of them. Something different must be introduced. Out of conceivable generalizations of (16.7) and (16.8), (16.10) and (16.11) appear to offer the most credible solutions if in these equations we simply omit the limiting process $h \to 0$, as prescribed by pure mathematics and classical mechanics. Instead of defining the optical frequency ν by derivatives we define it by a difference quotient. Deciding for this solution and putting

$$\nu_{12} = \frac{1}{h}(E_1 - E_2) \tag{16.12}$$

for the optical emission and absorption frequency, that is, for the frequency of the emitted or absorbed photon by the transition $E_1 \to E_2$, we are led to the Bohr frequency law. This law has been confirmed by experience in all known cases of transitions between electronic states.

The Correspondence Principle for Frequency and Intensity of Spectral Lines

The correspondence principle postulates an intimate connection to exist between quantities obtained from classical and quantum theory, as already mentioned in connection with the computation of frequencies from both theories. The principle may be expressed formally by stating that quantities obtained from quantum theory, and hence containing h, must transform into corresponding classical quantities by the limiting process $h \to 0$.

This is a purely formal process. A real correspondence is found, however, by another limiting process: that of using infinitely high quantum numbers. In an atom the energy levels of stationary electron orbits of high quantum numbers will be much more closely spaced than the energy levels of lower states. Hence the discontinuous character of atomic processes is much less pronounced for higher states. The correspondence principle presupposes that any difference between deductions from classical and quantum theories with respect to processes in an atomic system will gradually disappear as the quantum numbers for the states become sufficiently large.

The success of applying the correspondence principle to radiation frequencies of simple atomic models suggests that similar useful results must be obtainable for radiation intensities. Classically the radiation intensity from an atom in a given state must be computed by means of the Fourier representation of the coordinates as given in (15.29). If the atom possesses more than one electron, the amplitude of electronic vibrations must be summed up into the total electric dipole moment of the atom. For one electron and one

of its coordinates we may write

$$z = \sum_{m=-\infty}^{+\infty} z_m e^{2\pi i m w}, \tag{16.13}$$

where

$$mw = m_1 w_1 + m_2 w_2 + \cdots = (m_1 \nu_1 + m_2 \nu_2 + \cdots)t. \tag{16.14}$$

Equation 16.13 also may be written

$$z = z_0 + \sum_{m=1}^{\infty} 2\,|z_m| \cos 2\pi(mw + \delta_m), \tag{16.15}$$

δ_m being a phase factor caused by the fact that z_m and z_{-m} in general are complex numbers.

According to previous results [Part III, Section 22] the classical intensity of radiation from an oscillator with the frequency

$$\nu = m_1 \nu_1 + m_2 \nu_2 + \cdots \tag{16.16}$$

and amplitude $2\,|z_m|$ is

$$I_m = \frac{(2\pi\nu)^4 (2\,|z_m|)^2 e^2}{3c^3} = \frac{64\pi^4 \nu^4\,|z_m|^2\, e^2}{3c^3}. \tag{16.17}$$

The interpretation of this formula for the use in quantum theory is impeded by the fact that a quantum transition is related to two states, the initial and final states of the system. As to the question of frequency we naturally try to use the radiation frequency of the transition. As to the Fourier coefficient, probably neither of the coefficients of the two states can be used. We might try to replace it by the mean value of the coefficients of the upper and the lower states. In view of the favorable results obtained for the oscillator and rotator the best solution might possibly be to use Fourier coefficients of some fictitious intermediate state, say, that corresponding to mean values of angle variables for the two states.

In (16.13) and (16.15) we therefore put

$$z_m = z_{nn'}, \tag{16.18}$$

meaning thereby the Fourier coefficient for a given transition $n \to n'$, where according to the correspondence principle

$$m = \Delta n = n - n'. \tag{16.19}$$

More precisely we may state that

$$z_m = z_{(n+n')/2} = z_{nn'}.$$

This means that the Fourier coefficient z_m should be computed for the fictitious intermediate state $m = \frac{1}{2}(n + n')$.

Introducing this quantity in the formula (16.17), we obtain for the intensity of a spontaneously emitted spectral line

$$I_{nn'} = \frac{64\pi^4\nu^4 |z_{nn'}|^2 e^2}{3c^3}. \tag{16.20}$$

This is in fact the formula adopted in modern quantum theories, provided that the quantities $z_{nn'}$ are replaced by the well-defined matrix elements of wave mechanics. There are reasons to believe that the suggested method of computing these quantities from Fourier coefficients of partial vibrations will lead to results that are not very far from the truth.

Once more, it should be stressed, however, that everything that has been said above concerning the actual description of atomic systems is based on the supposition of quasiperiodic motion. The method therefore has not the same general character as wave-mechanical methods and can never compete with wave mechanics.

Having outlined a method for computation of radiation intensity in the manner as demonstrated above, we have at the same time created a basis for the previously mentioned selection and polarization rules. If a Fourier coefficient z_m or $z_{nn'}$ is zero, the radiation intensity corresponding to this partial vibration is also zero. If $x_{nn'} = 0$, $y_{nn'} = 0$, $z_{nn'} = 0$, this means that there is no radiation at all by the transition $n \to n'$. If only one of the three coefficients is different from zero, it follows from the corresponding principle that radiation is produced which is linearly polarized in accordance with what would be inferred from classical considerations. If only $x_{nn'} + iy_{nn'}$ or only $x_{nn'} - iy_{nn'}$ are different from zero, the result will be a spectral line circularly polarized if observed in direction parallel to the z-axis.

In the following sections we shall discuss these elements of the selection and polarization rules and apply them to particular atomic models.

17. THE KEPLER PROBLEM IN OLDER QUANTUM THEORY

The Kepler problem, the motion of an electron in the electrostatic field of an atomic nucleus with charge Ze, is a basic problem in atomic theory and will be discussed in detail in the following sections. These discussions will also comprise a complete review of the one- and two-dimensional rotator problem (the rigid and the free rotator). Together with the linear harmonic oscillator, these are the simplest problems met in quantum theory. The oscillator problem has been discussed earlier and it is not strictly necessary to repeat all of the details here. Because it is so extremely simple it may be advisable to give a short review of the problem as an introduction to the following more complex application of the general theory.

The Harmonic Oscillator

The expressions for kinetic and potential energy of a linear harmonic oscillator with mass m and frequency ν_0 are

$$T = \tfrac{1}{2}m\dot{x}^2, \qquad V = \tfrac{1}{2}m(2\pi\nu_0)^2x^2. \tag{17.1}$$

From the expression of momentum

$$p = \frac{\partial T}{\partial \dot{x}} = m\dot{x} \tag{17.2}$$

we obtain the Hamiltonian

$$H = \frac{1}{2m}p^2 + \frac{m}{2}(2\pi\nu_0)^2x^2 = E. \tag{17.3}$$

Hence

$$p = \pm[2mE - (2\pi\nu_0 m)^2x^2]^{1/2}. \tag{17.4}$$

Accordingly, the limit values of x are

$$x = \pm\frac{(2mE)^{1/2}}{2\pi\nu_0 m}.$$

Hence for the computation of the phase integral we put

$$x = \frac{(2mE)^{1/2}}{2\pi\nu_0 m}\cos u. \tag{17.5}$$

Observing that in the region $0 < x < \pi$ where dx is negative we have to use the negative sign for p in (17.4), we obtain

$$J = \oint p\,dx = \frac{2mE}{2\pi\nu_0 m}\int_0^{2\pi}\sin^2 u\,du = \frac{E}{\nu_0}. \tag{17.6}$$

According to our distinction between rotational and vibrational motion (libration) we put

$$J = (n + \tfrac{1}{2})h, \qquad n = 0, 1, \cdots. \tag{17.7}$$

Hence

$$E_n = (n + \tfrac{1}{2})h\nu_0. \tag{17.8}$$

Replacing E by $h\nu_0$ in (17.4) and choosing the sign in an appropriate way, we obtain the action function

$$S = -\int_{x_0}^{x}[2m\nu_0 J - (2\pi\nu_0 m)^2x^2]^{1/2}\,dx \tag{17.9}$$

The coordinate as an implicit function of time will then be given by the equation

$$w = \nu_0 t = \frac{\partial S}{\partial J} = -\int_{x_0}^{x}\frac{m\nu_0\,dx}{[2m\nu_0 J - (2\pi\nu_0 m)^2x^2]^{1/2}}. \tag{17.10}$$

Choosing the lower limit of the integral appropriately, say, $x_0 = x_{max}$, and using the substitution (17.5), we find

$$u = 2\pi w = 2\pi\nu_0 t. \tag{17.11}$$

The appearance of a single frequency ν_0 signifies that, according to the correspondence principle, the quantum transitions are $n \to n \pm 1$. Replacing E_n by $\frac{1}{2}(E_n + E_{n+1})$ in (17.5) and using half the amplitude, since $\cos u = \frac{1}{2}(e^{iu} + e^{-iu})$, we obtain an expression for the matrix element of wave mechanics

$$x_{n+1n} = \frac{1}{2\pi}\left[\frac{(n+1)h}{m\nu_0}\right]^{1/2} \tag{17.12}$$

which happens to give the strictly correct value.

Electron Orbits in the Hydrogen Atom

An electron of mass m is moving in the field of an atomic nucleus with a charge Z. The mass of the nucleus is considered large so as to prevent a perceptible motion of the nucleus. The kinetic and the potential energies are

$$T = \frac{m_0}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2), \qquad V = -\frac{Ze^2}{r}. \tag{17.13}$$

In spherical coordinates

$$x = r\sin\vartheta\cos\varphi, \qquad y = r\sin\vartheta\sin\varphi, \qquad z = r\cos\vartheta, \tag{17.14}$$

the kinetic energy transforms into

$$T = \frac{m_0}{2}(\dot{r}^2 + r^2\dot{\vartheta}^2 + r^2\sin^2\vartheta\dot{\varphi}^2). \tag{17.15}$$

Introducing corresponding momenta,

$$\begin{aligned} p_r &= \frac{\partial T}{\partial \dot{r}} = m_0\dot{r}, \\ p_\vartheta &= \frac{\partial T}{\partial \dot{\vartheta}} = m_0 r^2\dot{\vartheta}, \\ p_\varphi &= \frac{\partial T}{\partial \dot{\varphi}} = m_0 r^2\sin^2\vartheta\dot{\varphi}, \end{aligned} \tag{17.16}$$

we obtain the Hamiltonian

$$H = \frac{1}{2m_0}\left(p_r^2 + \frac{p_\vartheta^2}{r^2} + \frac{p_\varphi^2}{r^2\sin^2\vartheta}\right) - \frac{Ze^2}{r} = E. \tag{17.17}$$

The corresponding Hamilton-Jacobi equation is easily separated

$$S = S_r(r) + S_\vartheta(\vartheta) + S_\varphi(\varphi),$$
$$p_r = \frac{dS_r}{dr}, \qquad p_\vartheta = \frac{dS_\vartheta}{d\vartheta}, \qquad p_\varphi = \frac{dS_\varphi}{d\varphi}. \tag{17.18}$$

Equation 17.17 is satisfied by

$$p_\varphi = a_3$$
$$p_\vartheta = \pm\left(a_2^2 - \frac{a_3^2}{\sin^2\vartheta}\right)^{1/2}, \tag{17.19}$$
$$p_r = \pm\left(2m_0E + \frac{2m_0Ze^2}{r} - \frac{a_2^2}{r^2}\right)^{1/2},$$

E, a_2, and a_3 being constants of the motion. The action function can be written as

$$S = -\int_{r_0}^{r}\left(2m_0E + \frac{2m_0Ze^2}{r} - \frac{a_2^2}{r_2^2}\right)^{1/2} dr - \int_{\vartheta_0}^{\vartheta}\left(a_2^2 - \frac{a_3^2}{\sin^2\vartheta}\right)^{1/2} d\vartheta + a_3\varphi, \tag{17.20}$$

when r_0 and ϑ_0 are appropriately chosen. Since the first integration constant $a_1 = E$ is the energy, the constants c_i of (15.11) are

$$c_1 = \frac{\partial E}{\partial a_1} = 1, \qquad c_2 = \frac{\partial E}{\partial a_2} = 0, \qquad c_3 = \frac{\partial E}{\partial a_3} = 0. \tag{17.21}$$

Hence the integrated equations of motion are

$$t + b_1 = \frac{\partial S}{\partial E} = -\int_{r_0}^{r} \frac{m_0\,dr}{[2m_0E + (2m_0Ze^2/r) - (a_2^2/r^2)]^{1/2}}, \tag{17.22a}$$

$$b_2 = \frac{\partial S}{\partial a_2} = \int_{r_0}^{r} \frac{a_2/r^2}{[2m_0E + (2m_0Ze^2/r) - (a_2^2/r^2)]^{1/2}}\,dr - \int_{\vartheta_0}^{\vartheta} \frac{a_2\,d\vartheta}{(a_2^2 - a_3^2/\sin^2\vartheta)^{1/2}}, \tag{17.22b}$$

$$b_3 = \frac{\partial S}{\partial a_3} = \varphi + \int_{\vartheta_0}^{\vartheta} \frac{a_3/\sin^2\vartheta}{(a_2^2 - a_3^2/\sin^2\vartheta)^{1/2}}\,d\vartheta. \tag{17.22c}$$

Suppose the energy negative, $E < 0$. Then the interpretation of the above three equations can be rapidly facilitated by making use of the fact that the electron orbit is an ellipse. Put $\vartheta_0 = \pi/2$ corresponding to the nodal line, that is, the line of intersection between the orbital plane and the xy-plane of the coordinate system. Put further $r_0 = r_{\max}$ the maximal electron distance from the nucleus.

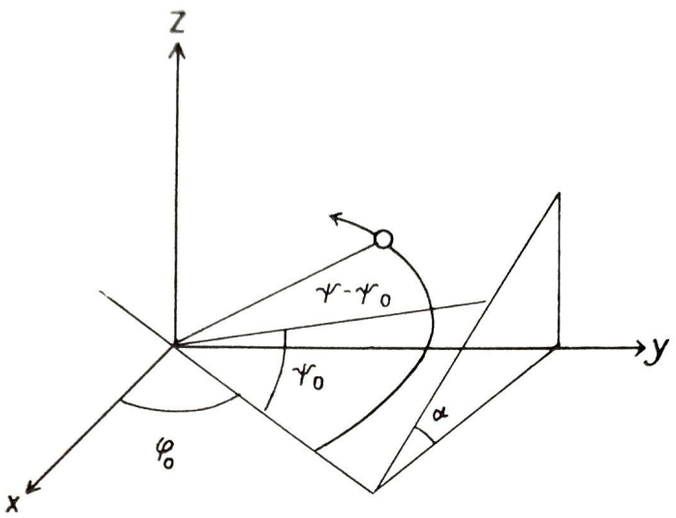

Fig. 2-8. Elliptic orbit of the electron in the hydrogen atom.

For further simplification of the integration process consider Fig. 2-8 with the orbital plane and the elliptic orbit of the electron. The angle α between the xy-plane and the orbital plane is given by

$$\cos \alpha = \frac{a_3}{a_2}, \qquad \sin \alpha = \frac{(a_2^2 - a_3^2)^{1/2}}{a_2}, \tag{17.23}$$

since a_2 is the total angular momentum and a_3 its z-component. If ψ is the polar angle of the electron in the orbital plane as measured from the nodal line and ψ_0 is the corresponding angle for the major axis of the ellipse pointing in the direction of the aphelion, we have the additional relations

$$\sin (\varphi - \varphi_0) = \cot \alpha \cot \vartheta, \qquad \sin \psi = \frac{\cos \vartheta}{\sin \alpha}, \tag{17.24}$$

φ_0 being the angle between the x-axis and the nodal line.

Beginning with (17.22c) the integrated equation is

$$b_3 = \varphi - \arcsin \frac{a_3}{(a_2^2 - a_3^2)^{1/2}} \cot \vartheta = \varphi - (\varphi - \varphi_0) = \varphi_0. \tag{17.25}$$

The second integral in (17.22b) is easily found to be

$$\arcsin \frac{a_2}{(a_2^2 - a_3^2)^{1/2}} \cos \vartheta = \arcsin \frac{\cos \vartheta}{\sin \alpha} = \psi. \tag{17.26}$$

To facilitate the computation of the first integral put

$$\frac{2m_0 E}{a_2^2} = -\frac{1}{b^2}, \qquad \frac{m_0 Z e^2}{a_2^2} = \frac{a}{b^2}, \qquad c^2 = a^2 - b^2 \tag{17.27}$$

which also implies that

$$E = -\frac{Ze^2}{2a}. \tag{17.28}$$

If, as mentioned above, $r_0 = r_{max} = c + a$, it is found that $b_2 = \psi_0$. From (17.22*b*) we therefore obtain

$$\psi - \psi_0 = -\int_{r\max}^{r} \frac{d(-1/r)}{[c^2/b^4 - (a/b^2 - 1/r)^2]^{1/2}} = \arccos \frac{b^2}{c}\left(\frac{a}{b^2} - \frac{1}{r}\right), \quad (17.29)$$

or

$$\frac{1}{r} = \frac{a}{b^2} - \frac{c}{b^2}\cos(\psi - \psi_0), \qquad r = \frac{b^2/a}{1 - c/a\cos(\psi - \psi_0)}, \quad (17.29a)$$

which is the well-known expression for an elliptic orbit in plane polar coordinates.

With the same constants as in (17.26) the integration of (17.22*a*) also becomes easy. We multiply the equation by the expression

$$\frac{a_2}{m_0 ab} = \frac{1}{m_0 a}\sqrt{-2m_0 E} = \frac{(-2E)^{3/2}}{Ze^2(m_0)^{1/2}} = 2\pi\nu_1 \quad (17.30)$$

and obtain

$$2\pi\nu_1(t + b_1) = -\int_{r\max}^{r} \frac{(r/a - 1) + 1}{[c^2 - (r - a)^2]^{1/2}}\,dr$$

$$= \arccos\frac{r - a}{c} + \frac{c}{a}\left[1 - \left(\frac{r - a}{c}\right)^2\right]^{1/2}. \quad (17.31)$$

(See Fig. 2-9.)

To describe in the simplest possible way the motion of the electron on its elliptic orbit as a function of time we introduce the *eccentric anomaly* u by writing

$$r = a + c\cos u. \quad (17.32)$$

Then (17.31) becomes

$$2\pi w_1 = 2\pi\nu_1(t + b_1) = u + \frac{c}{a}\sin u = u_1. \quad (17.33)$$

The quantity u_1, which is also an angle and increases linearly with time, is called *the mean anomaly*.

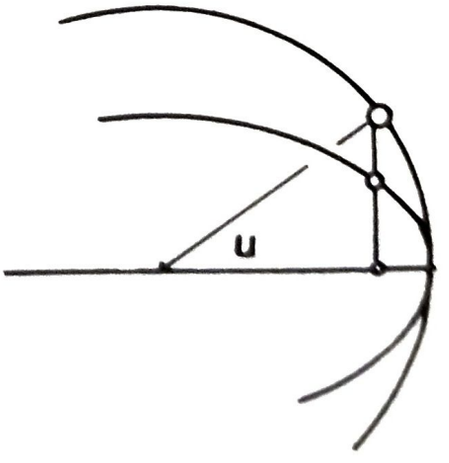

Fig. 2-9. Electron orbit as a function of the eccentric anomaly u.

In Cartesian coordinates x', y', in the orbital plane with the x'-axis in the direction of the major axis the elliptic orbit is given by the equations

$$x' = a\cos u + c, \qquad y' = b\sin u. \tag{17.34}$$

The coordinates of the electron thus are simple functions of the eccentric anomaly u, whereas their dependence on the mean anomaly u_1, hence on time, is rather complicated.

To express the elliptic constants in a more suitable way we introduce

$$a_1 = \frac{m_0 Z e^2}{(-2m_0 E)^{1/2}}, \tag{17.35}$$

that is,

$$E = -\frac{m_0 Z^2 e^4}{2a_1^{\,2}}, \tag{17.36}$$

and

$$a = \frac{a_1^{\,2}}{m_0 Z e^2}. \tag{17.37}$$

From (17.27) it follows that

$$b = \frac{a_1 a_2}{m_0 Z e^2}, \qquad \frac{b^2}{a} = \frac{a_2^{\,2}}{m_0 Z e^2}, \qquad c = \frac{a_1(a_1^{\,2} - a_2^{\,2})^{1/2}}{m_0 Z e^2}, \tag{17.38}$$

and from (17.29)

$$2\pi\nu_1 = \frac{m_0 Z^2 e^4}{a_1^{\,3}}. \tag{17.39}$$

18. CALCULATION OF PHASE INTEGRALS AND QUANTIZATION OF ELECTRON ORBITS IN THE KEPLER PROBLEM

Phase Integrals

For the purpose of obtaining energy values of stationary states and radiation frequencies, details of orbital motion are not needed. The standard method to be used here is that of complex integration. Meanwhile the integrals are nearly as easily obtained in the ordinary way of real integration by means of the quantities already introduced in the previous section.

If we split up the phase integral J_r in the most suitable way as follows

$$\begin{aligned} J_r = \oint p_r\, dr = &\oint \frac{(2m_0 E r + m_0 Z e^2)\, dr}{(2m_0 E r^2 + 2m_0 Z e^2 r - a_2^{\,2})^{1/2}} \\ &+ \oint \frac{m_0 Z e^2\, dr}{(2m_0 E r^2 + 2m_0 Z e^2 r - a_2^{\,2})^{1/2}} \\ &- \oint \frac{a_2^{\,2}\, d(-1/r)}{(2m_0 E + 2m_0 Z e^2/r - a_2^{\,2}/r^2)^{1/2}}, \end{aligned} \tag{18.1}$$

the first integral is zero. The second and third integrals can be suitably expressed by means of the eccentric anomaly u and the polar angle φ. Using (17.29), (17.31), and (17.35), we obtain

$$J_r = \frac{m_0 Z e^2}{(-2m_0 E)^{1/2}} \int_0^{2\pi} du - a_2 \int_0^{2\pi} d\psi = 2\pi(a_1 - a_2). \tag{18.2}$$

The integral J_ϑ can be similarly simplified by means of the angles ψ and φ,

$$J_\vartheta = \oint p_\vartheta \, d\vartheta = \oint \frac{a_2^2 \, d\vartheta}{(a_2^2 - a_3^2/\sin^2\vartheta)^{1/2}} - \oint \frac{a_3^2/\sin^2\vartheta}{(a_2^2 - a_3^2/\sin^2\vartheta)^{1/2}} d\vartheta$$

$$= a_2 \int_0^{2\pi} d\psi - a_3 \int_0^{2\pi} d\varphi = 2\pi(a_2 - a_3). \tag{18.3}$$

Finally

$$J_\varphi = 2\pi a_3. \tag{18.4}$$

Quantum Numbers

A quantization of these action variables implies the introduction of three independent quantum numbers n_r, n_ϑ, n_φ, the *radial*, *polar*, and *equatorial* quantum numbers. The latter is integral; the two former numbers are half-quantum numbers owing to the librational character of the motion in the coordinates r and ϑ. It is more convenient, however, to introduce alternative action variables and quantum numbers

$$J_1 = J_r + J_\vartheta + J_\varphi = 2\pi a_1 = nh, \tag{18.5a}$$

$$J_2 = \quad J_\vartheta + J_\varphi = 2\pi a_2 = (l + \tfrac{1}{2})h, \tag{18.5b}$$

$$J_3 = \quad J_\varphi = 2\pi a_3 = mh. \tag{18.5c}$$

Here

$$n = n_r + \tfrac{1}{2} + l + \tfrac{1}{2} = n_r + l + 1 \tag{18.6}$$

is a positive integer $n \geqq 1$, which is called the *principal* or *energy* quantum number, and

$$l = n_\vartheta - \tfrac{1}{2} + m \tag{18.7}$$

is the *azimuthal* quantum number which is also a positive integer, including zero, and smaller than n. Finally the equatorial or "magnetic" quantum number m is a positive or negative integer, $|m| \leqq l$. By a given principal quantum number n there are the following possibilities for l and m,

$$l = 0, 1, \cdots, n-1, \qquad m = -l, \cdots, -1, 0, 1, \cdots, l. \tag{18.8}$$

By (18.5a) and (17.35)

$$E = -\frac{2\pi^2 m_0 Z^2 e^4}{J_1^2} = -\frac{2\pi^2 m_0 Z^2 e^4}{n^2 h^2} \tag{18.9}$$

or, with the value already found for the Rydberg constant,

$$E_n = -\frac{Z^2 Rh}{n^2}. \tag{18.10}$$

In this representation the energy depends only on the action variable J_1, hence on the principal quantum number n. This is a consequence of the coincidence of the main frequencies of the motion in the coordinates r, ϑ, and φ, $\nu_r = \nu_\vartheta = \nu_\varphi$. With the new action variables of (18.5) two of the corresponding frequencies are zero,

$$\nu_2 = \frac{\partial E}{\partial J_2} = 0, \qquad \nu_3 = \frac{\partial E}{\partial J_3} = 0. \tag{18.11}$$

This means that their canonical conjugate or angle variables are constants

$$u_2 = 2\pi w_2 = \psi_0, \qquad u_3 = 2\pi w_3 = \varphi_0. \tag{18.12}$$

In this representation a single frequency different from zero remains,

$$\nu_1 = \frac{\partial E}{\partial J_1} = \frac{4\pi^2 m_0 Z^2 e^4}{J_1^3} = \frac{m_0 Z^2 e^4}{2\pi a_1^3}. \tag{18.13}$$

This is the same frequency as already given in (17.30) and (17.39).

The elliptic constants of (17.37) and (17.38) depend on the above quantum number as follows,

$$\begin{aligned} a &= \frac{J_1^2}{4\pi^2 m_0 Z e^2} = \frac{h^2 n^2}{4\pi^2 m_0 Z e^2} = n^2 \frac{a_H}{Z}, \\ b &= \frac{J_1 J_2}{4\pi^2 m_0 Z e^2} = n(l + \tfrac{1}{2}) \frac{a_H}{Z}, \qquad c = [n^2 - (l + \tfrac{1}{2})^2]^{1/2} \frac{a_H}{Z}. \end{aligned} \tag{18.14}$$

Mean Values in Older Quantum Theory

In atomic theory mean values of various quantities are frequently needed, in particular mean values of powers of the electronic distance from the nucleus. It will be instructive to calculate such quantities from the Bohr theory and to compare them with values obtained by wave mechanics.

We first need a relation between the polar angle ψ of the electron and the mean anomaly u_1. Remembering the constancy of angular momentum and considering the integral

$$\oint r^2 \, d\psi = 2\pi ab, \tag{18.15}$$

which is twice the elliptic area, we easily see that the relation is

$$du_1 = \frac{r^2}{ab} \, d\psi. \tag{18.16}$$

Mean values of negative powers of r as $\overline{r^{-2}}$, $\overline{r^{-3}}$, are obtained by using the elliptic equation (17.29*a*). For $\overline{r^{-1}}$, $\bar{r}$, $\overline{r^2}$, $\cdots$, however, (17.32) and (17.33) are needed. For instance,

$$\begin{aligned}\overline{r^{-2}} &= \frac{1}{2\pi}\int_0^{2\pi}\frac{du_1}{r^2} = \frac{1}{2\pi ab}\int_0^{2\pi} d\psi = \frac{1}{ab}\\ \overline{r^{-3}} &= \frac{1}{2\pi ab}\int_0^{2\pi}\frac{d\psi}{r} = \frac{1}{b^3}.\end{aligned} \tag{18.17}$$

From the known values

$$a = \frac{n^2 a_H}{Z}, \qquad b = n(l+\tfrac{1}{2})\frac{a_H}{Z}, \tag{18.18}$$

we obtain

$$\overline{r^{-2}} = \frac{Z}{{a_H}^2}\cdot\frac{1}{n^3(l+\frac{1}{2})}, \qquad \overline{r^{-3}} = \frac{Z^3}{{a_H}^3}\cdot\frac{1}{n^3(l+\frac{1}{2})^3}. \tag{18.19}$$

The corresponding mean values of wave mechanics are

$$\overline{r^{-2}} = \frac{Z}{{a_H}^2}\cdot\frac{1}{n^3(l+\frac{1}{2})}, \qquad \overline{r^{-3}} = \frac{Z^3}{{a_H}^3}\cdot\frac{1}{n^3 l(l+\frac{1}{2})(l+1)}. \tag{18.20}$$

Similarly by (17.32) and (17.33), putting $c/a = \varepsilon$, we find

$$\begin{aligned}\overline{r^{-1}} &= \frac{1}{2\pi}\int_0^{2\pi}\left(1+\frac{c}{a}\cos u\right)\frac{du}{r} = \frac{1}{a},\\ \bar{r} &= \frac{a}{2\pi}\int_0^{2\pi}\left(1+\frac{c}{a}\cos u\right)^2 du = a\left(1+\frac{1}{2}\varepsilon^2\right),\\ \overline{r^2} &= \frac{a^2}{2\pi}\int_0^{2\pi}\left(1+\frac{c}{a}\cos u\right)^3 du = a^2\left(1+\frac{3}{2}\varepsilon^2\right).\end{aligned} \tag{18.21}$$

Again, introducing elliptic constants according to (18.14),

$$\begin{aligned}\overline{r^{-1}} &= \frac{Z}{a_H n^2},\\ \bar{r} &= \frac{a_H}{Z}\left\{n^2+\frac{1}{2}[n^2-(l+\tfrac{1}{2})^2]\right\},\\ \overline{r^2} &= \frac{{a_H}^2}{Z^2}n^2\left\{n^2+\frac{3}{2}[n^2-(l+\tfrac{1}{2})^2]\right\}.\end{aligned} \tag{18.22}$$

The values obtained in wave mechanics are

$$\overline{r^{-1}} = \frac{Z}{a_H n^2},$$

$$\bar{r} = \frac{a_H}{Z}\left\{n^2 + \frac{1}{2}[n^2 - l(l+1)]\right\}, \tag{18.23}$$

$$\overline{r^2} = \frac{a_H^2}{Z^2} n^2\left\{n^2 + \frac{3}{2}\left[n^2 - \left[l(l+1) - \frac{1}{3}\right]\right]\right\}.$$

Hence mean values as obtained from the Bohr theory are not very different from those obtained by wave mechanics. The difference consists mainly in replacing powers of $(l + \frac{1}{2})$ by somewhat different expressions, say, $(l + \frac{1}{2})^2$ by $l(l+1)$, $(l + \frac{1}{2})^3$ by $l(l + \frac{1}{2})(l + 1)$, and so forth.

Problems

1. From (17.4) calculate by complex integration the phase integral for the harmonic oscillator. In order to simplify the problem first make the substitution
$$x = \xi(2mE)^{1/2}/2\pi\nu_0 m.$$
2. Calculate by complex integration the integral
$$\oint\left(-A + \frac{2B}{r} - \frac{C}{r^2}\right)^{1/2} dr$$
and show that it equals $2\pi(B/\sqrt{A} - \sqrt{C})$.
3. Apply this result to the radial phase integral of the Kepler problem as given by p_r in (17.19).
4. Substitute $\xi = \cos\vartheta$ in p_ϑ (17.19) and calculate by complex integration the phase integral $\oint p_\vartheta\, d\vartheta$.
5. Compare (17.29*a*) and (17.32). Find the equation connecting the eccentric anomaly u and the polar angle ψ of the elliptic orbit of the electron. Find the first-order differential equation connecting the two quantities as expressed in u, ψ, or r.
6. Find by complex integration, extending the path of integration toward infinity, the value of the integral
$$\oint \frac{dr}{(-A + 2Br - Cr^2)^{1/2}}$$
and show that it equals $2\pi/\sqrt{C}$. Apply the result to the two last integrals in (18.1) and verify the result (18.2).
7. Substitute $\xi = \cos\vartheta$ in (18.3) and calculate the two integrals by complex integration.
8. Extend the mean value calculations of (18.16)–(18.22) to $\overline{r^{-4}}$ and $\overline{r^3}$.

19. ELECTRON ORBITS IN MAGNETIC AND NON-COULOMB FIELDS

A homogeneous magnetic field H in the direction of the z-axis can be expressed by the vector potential

$$A_x = -\tfrac{1}{2}yH, \qquad A_y = \tfrac{1}{2}xH, \qquad A_z = 0. \tag{19.1}$$

In spherical coordinates the single component different from zero is

$$A_\varphi = A_y \cos\varphi - A_x \sin\varphi = \tfrac{1}{2}Hr \sin\vartheta. \tag{19.2}$$

To obtain the Hamiltonian for a particle of charge $(-e)$ in a combined Coulomb and magnetic field we must, in the Hamiltonian (17.17), replace $(p_\varphi/r\sin\vartheta)^2$ by

$$\left(\frac{p_\varphi}{r\sin\vartheta} + \frac{e}{c}\frac{H}{2} r\sin\vartheta\right)^2 = \frac{p_\varphi^{\,2}}{r^2\sin^2\vartheta} + \frac{eH}{c}p_\varphi + \left(\frac{e}{c}\frac{H}{2}\right)^2 r^2\sin^2\vartheta, \tag{19.3}$$

The last term which represents the "quadratic" Zeeman effect is insignificant for moderate fields and is frequently omitted; hence usually only the second term giving the ordinary Zeeman effect is added to the square momentum p^2 of the ordinary Hamiltonian.

Another generalization of the Kepler problem consists of replacing the Coulomb field by a somewhat different central field containing an additive term of a non-Coulomb type. This causes the elliptic orbit to change into a rosette-like orbit. If the deviation from a Coulomb field is small, the orbit will approximately be an ellipse with its major axis rotating in the orbital plane. If the field deviates from the Coulomb field according to the law A/r^2, the particular result will be true that the orbit is an ellipse, which, however, rotates with a not strictly uniform speed. We therefore limit our discussion to this case and put

$$V = -\frac{Ze^2}{r} - \frac{h^2}{8\pi^2 m_0}\frac{\gamma}{r^2}. \tag{19.4}$$

In the last term the reason for choosing a multiplication factor of the above form will be obvious later.

Hence for a combined magnetic and non-Coulomb field the energy function and energy equation can be written as

$$\frac{1}{2m_0}\left[p_r^{\,2} + \frac{p_\vartheta^{\,2}}{r^2} - \left(\frac{h}{2\pi}\right)^2\frac{\gamma}{r^2} + \frac{p_\varphi^{\,2}}{r^2\sin^2\vartheta}\right] - \frac{Ze^2}{r} + \frac{eH}{2m_0c}p_\varphi = E, \tag{19.5}$$

where φ is again a cyclic coordinate and p_φ is a constant. By separation of the

corresponding Hamilton-Jacobi equation we obtain

$$\begin{aligned} p_\varphi &= a_3, \\ p_\vartheta^2 - \frac{p_\varphi^2}{\sin^2\vartheta} &= a_2^2, \\ E - \frac{eH}{2m_0c}\,p_\varphi &= -\frac{m_0Z^2e^4}{2a_1^2}. \end{aligned} \tag{19.6}$$

In the following computation of phase integrals we repeat some of the equations from previous sections:

$$\begin{aligned} J_\varphi &= 2\pi a_3, \\ J_\vartheta &= 2\pi(a_2 - a_3), \\ J_r &= 2\pi\left\{a_1 - \left[a_2^2 - \left(\frac{h}{2\pi}\right)^2\gamma\right]^{1/2}\right\}, \end{aligned} \tag{19.7}$$

or

$$\begin{aligned} J_\varphi = J_3 &= 2\pi a_3, \\ J_\vartheta + J_\varphi = J_2 &= 2\pi a_2, \\ J_r + J_\vartheta + J_\varphi = J_1 &= 2\pi\left\{a_1 + a_2 - \left[a_2^2 - \left(\frac{h}{2\pi}\right)^2\gamma\right]^{1/2}\right\}. \end{aligned} \tag{19.8}$$

Conversely

$$a_3 = \frac{J_3}{2\pi}, \qquad a_2 = \frac{1}{2\pi}J_2, \qquad a_1 = \frac{1}{2\pi}(J_1 - J_2 + \sqrt{J_2^2 - h^2\gamma}\,. \tag{19.9}$$

From the third equation of (19.6) and (19.9) we obtain

$$E = -\frac{2\pi^2 m_0 e^4 Z^2}{[J_1 - J_2 + (J_2^2 - h^2\gamma)^{1/2}]^2} + \frac{eH}{4\pi m_0 c}J_3. \tag{19.10}$$

For these modified fields the frequencies ν_2 and ν_3 are no longer zero. For instance

$$\nu_3 = \frac{\partial E}{\partial J_3} = \frac{eH}{4\pi m_0 c}, \qquad \varphi_0(t) = u_3 = 2\pi\nu_3 t + b_3. \tag{19.11}$$

Here ν_3 is the Larmor frequency of the precession of the orbital plane around the axis z of the magnetic field, as shown by the above expression for the angle φ_0 between the nodal line and the x-axis. Next

$$\nu_2 = \frac{\partial E}{\partial J_2} = (\kappa - 1)\nu_1, \qquad \kappa = \frac{J_2}{(J_2^2 - h^2\gamma)^{1/2}}, \tag{19.12}$$

is the rotation frequency of the elliptic axis in the orbital plane. This rotation, however, is not strictly even. The polar angle $\psi - \psi_0$ in (17.29) differs by a periodic function $f(u_1)$ from the mean anomaly u_1 which is a linear function of time. Hence (17.29) can be written

$$\arccos \frac{b^2}{c}\left(\frac{a}{b^2} - \frac{1}{r}\right) = u_1 + f(u_1), \qquad u_1 = 2\pi\nu_1 t. \tag{19.13}$$

The periodic function $f(u_1)$ expresses the libration of the polar angular velocity $\dot{\psi}$ in a purely Coulomb field.

The orbit of the electron in a non-Coulomb field can be determined by the equation $w_2 = \partial S/\partial J_2$. This leads to the following equation for the polar angle.

$$\psi - \Psi_0 = \kappa[2\pi\nu_1 t + f(u_1)] \tag{19.13a}$$

where Ψ_0 is a time-independent angle which is different from the polar angle $\psi_0(t)$ of the major elliptic axis. Hence by (19.13) the elliptic equation in polar coordinates is

$$r = \frac{b^2/a}{1 - (c/a)\cos[(\psi - \Psi_0)/\kappa]}. \tag{19.13b}$$

This equation differs from that of Keplerian motion merely by the factor κ. To obtain an angle representing at any instant the rotation angle $\psi_0(t)$ of the major elliptic axis, we write

$$\frac{\psi - \Psi_0}{\kappa} = \psi - \psi_0 = \psi - \Psi_0 - (\psi_0 - \Psi_0), \tag{19.14}$$

or by (19.12) and (19.13a),

$$\psi_0 - \Psi_0 = \left(1 - \frac{1}{\kappa}\right)(\psi - \Psi_0) = 2\pi\nu_2 t + (\kappa - 1)f(u_1), \tag{19.14a}$$

or finally,

$$\psi_0(t) = 2\pi\nu_2 t + \Psi_0 + (\kappa - 1)f(u_1). \tag{19.14b}$$

Because of $\kappa - 1 = \nu_2/\nu_1 \ll 1$ the deviation of the elliptic axis from a uniform rotational motion is usually entirely insignificant. Hence we have the following simple picture of electronic motion in a combined non-Coulomb and magnetic field: The orbital plane is rotating about the magnetic field and the major axis of the elliptic electron orbit precesses with practically constant speed in the orbital plane.

If in (19.10) we put $J_1 = nh$, $J_2 = (l + \frac{1}{2})h$, $J_3 = mh$, we obtain the quantized energy value of the electron in a combined magnetic and non-Coulomb

field as a function of the quantum numbers n, l, m:

$$E_{nlm} = -\frac{Z^2Rh}{\{n-(l+\frac{1}{2})+[(l+\frac{1}{2})^2-g]^{\frac{1}{2}}\}^2}+\frac{ehH}{4\pi m_0 c}m. \tag{19.15}$$

The quantity

$$\mu_0 = \frac{eh}{4\pi m_0 c} \tag{19.16}$$

has the dimension of a magnetic dipole and is called the *Bohr magneton.*

The Relativistic Fine-Structure Formula

In relativistic mechanics, the Hamiltonian of the Kepler problem with no magnetic field is

$$H = c(p^2 + m_0{}^2c^2)^{\frac{1}{2}} - \frac{Ze^2}{r} = E. \tag{19.17}$$

It is important to note that mathematically this equation can be treated by the same method as for the non-Coulomb field. We solve (19.17) with respect to p^2,

$$p^2 = \frac{1}{c^2}\left(E+\frac{Ze^2}{r}\right)^2 - m_0{}^2c^2, \tag{19.18}$$

and rearrange it into

$$\frac{p^2}{2m_0} - \frac{E}{m_0c^2}\cdot\frac{Ze^2}{r} - \frac{Z^2e^4}{2m_0c^2r^2} = \frac{E^2-m_0{}^2c^4}{2m_0c^2}. \tag{19.19}$$

This is formally the same equation as for the non-Coulomb field if in the latter we replace the total energy E of the ordinary Coulomb field by the right-hand side of (19.19) and the nuclear charge number Z by

$$Z' = \frac{E}{m_0c^2}Z. \tag{19.20}$$

The additional energy of r^{-2}-type corresponds to the value

$$\gamma = \left(\frac{2\pi Ze^2}{hc}\right)^2 = Z^2\alpha^2, \tag{19.21}$$

of the constant γ in (19.4),

$$\alpha = \frac{2\pi e^2}{hc} \approx \frac{1}{137} \tag{19.22}$$

being the Sommerfeld fine-structure constant.

Hence, using (19.15), we can express the quantized relativistic energy by the formula

$$m_0c^2\frac{E^2-m_0{}^2c^4}{2E^2} = -\frac{Z^2Rh}{\{n-(l+\frac{1}{2})+[(l+\frac{1}{2})^2-Z^2\alpha^2]^{\frac{1}{2}}\}^2}. \tag{19.23}$$

In the famous fine-structure formula of Sommerfeld from 1916 the secondary quantum number

$$k = 1, 2, 3, \cdots, n \tag{19.24}$$

takes the place of $l + \frac{1}{2}$ in the above formula. Sommerfeld's formula is numerically true in spite of his using a quantization of librational motion which, according to the above discussion, is not justified. Using the more reliable method above, partly borrowed from wave mechanics, we obtain an incorrect formula. This is in reality not a failure, however. In fact, at this stage there must be a discrepancy if we are to obtain final agreement with experience when taking into account the spin of the electron. To state it in the shortest way: The spinning electron causes the term $l + \frac{1}{2}$ to change into l and $l + 1$, thus doubling the states of the hydrogen atom and its homologous ions: He^+, Li^{++}, and so forth. These double states, which are again separated in non-Coulomb fields, are easily observed in X-ray spectroscopy. The Sommerfeld formula is therefore insufficient, in the sense that it replaces $l + \frac{1}{2}$ only by $k = l + 1$.

The formula (19.23) can be expanded in powers of $Z^2\alpha^2$. If $E = E' + m_0c^2$, and hence E' the energy of the electron after subtraction of the rest energy m_0c^2, we obtain

$$\begin{aligned} E' &= -\frac{(1 + E'/m_0c^2)^2}{1 + E'/2m_0c^2} \cdot \frac{Z^2Rh}{n^2}\left[1 + \frac{Z^2\alpha^2}{n(l + \frac{1}{2})}\right] \\ &= -\frac{Z^2Rh}{n^2}\left[1 + \frac{Z^2\alpha^2}{n^2}\left(\frac{n}{l + \frac{1}{2}} - \frac{3}{4}\right)\right]. \end{aligned} \tag{19.25}$$

The Effect of the Electron Spin

To explain some characteristic individual features of atomic line spectra Uhlenbeck and Goudsmit in 1925 put forward the hypothesis of the spinning electron. Because of its eigenrotation the spinning electron has a mechanical angular momentum or spin which is $\frac{1}{2}h/2\pi$ or half the ordinary unit $h/2\pi$ of orbital angular momentum. The magnetic dipole moment, on the other hand, has proved to be a full Bohr magneton

$$\mu_0 = \frac{eh}{4\pi m_0 c}, \tag{19.26}$$

and not, as might possibly have been expected, only half that unit. Hence the ratio of magnetic moment and spin of the electron eigenrotation is e/m_0c as compared to $e/2m_0c$ for orbital motion.

The electron has a relative motion with respect to the atomic nucleus. According to the principle of relativity it should then be subject to a magnetic field produced by the nucleus, as though it were moving with velocity $-\mathbf{v}$ opposite in direction to the velocity $\mathbf{v}$ of the electron. It is not strictly

correct, however, to treat the problem in this simple way when the electron is performing a rotational motion instead of moving with constant velocity. Thomas and Frenkel endeavored to perform a closer analysis of particular difficulties encountered in this problem and have made it plausible that one should rather consider a field corresponding to half the above velocity of the nucleus. By Biot-Savart's law the field acting on the electron is therefore

$$\mathbf{H} = -\frac{Ze\mathbf{v}}{2c} \times \frac{\mathbf{r}}{r^3} = \frac{Ze}{2m_0cr^3}(\mathbf{r} \times m_0\mathbf{v}) = \frac{Ze\mathbf{m}}{2m_0cr^3}, \tag{19.27}$$

$\mathbf{m}$ denoting the orbital angular momentum

$$\mathbf{m} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times m_0\mathbf{v}. \tag{19.28}$$

Putting for the magnetic moment of the electron

$$\mu_s = -\frac{e}{m_0c}\mathbf{m}_s, \tag{19.29}$$

$\mathbf{m}_s$ being the vectorial spin of the *negatively* charged electron, the additional magnetic energy becomes

$$\Delta E = -\mathbf{H}\mu_s = \frac{Ze^2}{2m_0{}^2c^2} \cdot \frac{\mathbf{m}\mathbf{m}_s}{r^3}. \tag{19.30}$$

To the first approximation we write

$$\mathbf{m}\mathbf{m}_s = \pm\frac{1}{2}\left(l + \frac{1}{2}\right)\left(\frac{h}{2\pi}\right)^2, \qquad \overline{\left(\frac{1}{r^3}\right)} = \frac{Z^3}{a_H{}^3} \cdot \frac{1}{n^3(l + \frac{1}{2})^3}, \tag{19.31}$$

corresponding, respectively, to the parallel and antiparallel addition of spin and orbital angular momentum of the electron, and to the mean value $\overline{r^{-3}}$ of the older quantum theory, (18.19). Noting that

$$\frac{Ze^2}{2m_0{}^2c^2} \cdot \left(\frac{h}{2\pi}\right)^2 \cdot \frac{Z^3}{a_H{}^3} = \frac{Z^4e^2}{2a_H} \cdot \left(\frac{2\pi e^2}{hc}\right)^2 = Z^4Rh\alpha^2, \tag{19.32}$$

the relativistic formula (19.25) must be changed into

$$E' = -\frac{Z^2Rh}{n^2}\left\{1 + \frac{Z^2\alpha^2}{n^2}\left[\frac{n}{l + \frac{1}{2}} \mp \frac{n}{2(l + \frac{1}{2})^2} - \frac{3}{4}\right]\right\}. \tag{19.33}$$

The first two terms of the inner bracket may be written

$$\frac{n(l + \frac{1}{2} \mp \frac{1}{2})}{(l + \frac{1}{2})^2}.$$

If, as a concession to wave mechanics, we change the denominator into

$l(l+1)$, the above term reads:

$$\frac{n}{l+\frac{1}{2}\pm\frac{1}{2}}=\frac{n}{k}, \qquad k=l+1,\ l. \tag{19.34}$$

We have now arrived at the approximate form

$$E'=-\frac{Z^2Rh}{n^2}\left[1+\frac{Z^2\alpha^2}{n^2}\left(\frac{n}{k}-\frac{3}{4}\right)\right], \tag{19.35}$$

of the Sommerfeld fine-structure formula. Returning to the nonexpanded formula in (19.23) and observing that $2Rh/m_0c^2=\alpha^2$, we write

$$\frac{E^2-m_0{}^2c^4}{E^2}=-\frac{Z^2\alpha^2}{[n-k+(k^2-Z^2\alpha^2)^{1/2}]^2}. \tag{19.36}$$

This formula might have been obtained by putting $J_2=kh$ in place of $J_2=(l+\frac{1}{2})h$. According to wave mechanics this is not permitted. The inaccurate formula of ordinary wave mechanics can be modified so as to agree with the true fine structure formula only on the basis of the concept of the spinning electron. Accepting the integer k as a secondary quantum number, we assume two different values $k=l+1,\ l$, as contrasted to the single value $k=l+1$ of the original Sommerfeld theory.

The result obtained in (19.34) and (19.35) is based on a minor correction of the denominator $(l+\frac{1}{2})^2$ in (19.23). To obtain a more rigorous proof we rely upon the more modern form of quantum theory. The scalar product of two vectors **A** and **B** obeys the equation

$$2\mathbf{AB}=\mathbf{C}^2-\mathbf{A}^2-\mathbf{B}^2, \qquad \mathbf{C}=\mathbf{A}+\mathbf{B}. \tag{19.37}$$

For the mean value of the corresponding scalar product of **m** and $\mathbf{m}_s$ quantum mechanics provides the formula

$$2\mathbf{m}\mathbf{m}_s=\left(\frac{h}{2\pi}\right)^2[(l\pm s)(l+1\pm s)-l(l+1)-s(s+1)], \tag{19.38}$$

where $s=\frac{1}{2}$. Hence we have to replace (19.31) by

$$\mathbf{m}\mathbf{m}_s=\frac{1}{2}\left(\frac{h}{2\pi}\right)^2\cdot\begin{bmatrix} l \\ -(l+1)\end{bmatrix}. \tag{19.39}$$

If we also use the wave-mechanical formula (18.20) for $\overline{r^{-3}}$, that is, replace the denominator $(l+\frac{1}{2})^3$ by $l(l+\frac{1}{2})(l+1)$, the first two terms of the inner bracket in (19.33) transform into

$$\frac{n}{l+\frac{1}{2}}\mp\frac{n}{2(l+\frac{1}{2})(l+\frac{1}{2}\pm\frac{1}{2})}=\frac{n}{l+\frac{1}{2}\pm\frac{1}{2}}=\frac{n}{k}, \tag{19.40}$$

in accordance with (19.34) and (19.35).

The Anomalous Zeeman Effect and the Landé Formula

In correcting for electron spin in the relativistic formula we, in fact, presupposed two mutually counterbalancing effects: the factor $\frac{1}{2}$ in formula (19.27) of the effective magnetic field acting on the electron owing to its relative motion, and next the doubled value of the magnetic moment of the electron, that is, a full Bohr magneton instead of half a magneton. These suppositions call for more detailed arguments.

Magnetic momenta of atoms and molecules can be measured by the molecular beam method, developed by O. Stern and W. Gerlach, which measures the deviation in an inhomogeneous magnetic field of a beam of thermal atoms or molecules that emerge from an aperture or slit in an oven of high temperature. Alkali atoms are best fitted for the purpose of measuring the magnetic moment of the electron, since in the ground state of these atoms their magnetic moment is entirely because of the eigenspin of the electron. The magnetic moment of free hydrogen atoms in the ground state has also been measured. These measurements have confirmed without exception the correctness of the above value of the electronic magnetic moment.

This value has also been confirmed by an entirely different observation, the *anomalous Zeeman effect*. (See Fig. 2-10.) As a matter of fact, it was this particular anomaly in the magnetic separation of spectral lines that led Uhlenbeck and Goudsmit to the idea of the spinning electron.

If we accept the hypothesis of the spinning electron, the orbital angular momentum is no longer a constant of the motion. In this respect it is replaced by the total angular momentum

$$\mathbf{M} = \mathbf{m} + \mathbf{m}_s. \tag{19.41}$$

In a magnetic field this vector angular momentum will be slowly rotating around the axis of the magnetic field, its component M_z on the axis being

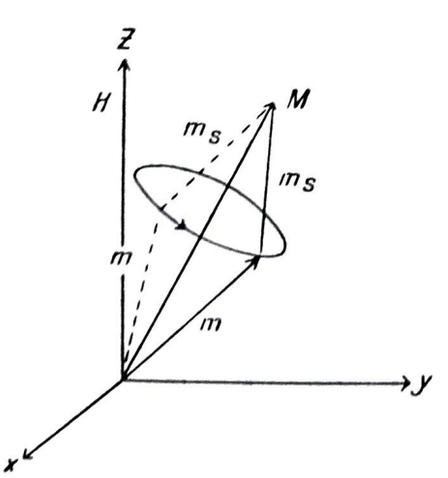

Fig. 2-10. The anomalous Zeeman effect as a consequence of the anomalous magnetic moment of the spinning electron.

constant. Hence the angle ϑ subtended by **M** and **H** is constant and given by

$$\cos\vartheta = \frac{M_s}{|\mathbf{M}|}. \tag{19.42}$$

On the other hand, orbital spin and electron spin are rotating much quicker around their sum vector **M**. Hence it suffices to compute their components in the direction of the total angular momentum which are found to be

$$\frac{\mathbf{mM}}{|\mathbf{M}|} = \frac{\mathbf{M}^2 + \mathbf{m}^2 - \mathbf{m}_s^2}{2\,|\mathbf{M}|}, \qquad \frac{\mathbf{m}_s\mathbf{M}}{|\mathbf{M}|} = \frac{\mathbf{M}^2 + \mathbf{m}_s^2 - \mathbf{m}^2}{2\,|\mathbf{M}|}, \tag{19.43}$$

respectively. If these are added, the result will be $|\mathbf{M}|$. The addition of magnetic momenta yields quite a different result, the sum vector being generally not in the direction of **M**. The sum component in that direction is easily found to be

$$\frac{e}{2m_0c}\left(\frac{\mathbf{M}^2 + \mathbf{m}^2 - \mathbf{m}_s^2}{2\,|\mathbf{M}|} + \frac{\mathbf{M}^2 + \mathbf{m}_s^2 - \mathbf{m}^2}{|\mathbf{M}|}\right) = \frac{e\,|\mathbf{M}|}{2m_0c}\left(1 + \frac{\mathbf{M}^2 + \mathbf{m}_s^2 - \mathbf{m}^2}{2\mathbf{M}^2}\right). \tag{19.44}$$

The quantized values of **M** are

$$|\mathbf{M}| = \frac{h}{2\pi}(j + \tfrac{1}{2}), \qquad M_z = \frac{h}{2\pi}m_j, \tag{19.45}$$

$j = l \pm \frac{1}{2}$ and $m_j = -j, \cdots, -\frac{1}{2}, \frac{1}{2}, \cdots, j$, being quantum numbers referring to total angular momentum. In a magnetic field the additional magnetic energy therefore becomes

$$E_m = \frac{ehH}{4\pi m_0 c} m_j g, \tag{19.46}$$

g being the reputed Landé g-factor which was first proposed by Landé on the basis of empirical knowledge of the anomalous Zeeman effect. Using wave-mechanical values of square angular momenta [compare (33.14)] we obtain by (19.44) the expression

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}, \tag{19.47}$$

where $s = \frac{1}{2}$. In the case of more than one electron an analogous formula is valid, in which the quantum numbers j, l, s for a single electron are replaced by the corresponding group of quantum numbers J, L, S, $J = |L - S|, \cdots, L + S - 1, L + S$. The value of S depends on the number of electrons. In the case of two electrons it may have the values $S = 0$ and $S = 1$, for three electrons $S = \frac{1}{2}, \frac{3}{2}$, for four electrons $S = 0, 1, 2$, and so on.

The value $S = \frac{1}{2}$ for one electron or three electrons (hydrogen, lithium) leads to doublet terms, the value $S = 1$ to triplets, and so on. The case $S = 0$ appears for an even number of electrons (helium), leading to singlet terms and $J = L$. In this case the Landé g-factor is 1 and the Zeeman effect is normal, that is, in accordance with the simple Lorentz theory.

20. ANHARMONIC OSCILLATORS AND MOLECULAR POTENTIALS

The harmonic oscillator affords the simplest example of atomic vibration within a molecule or a crystal lattice. Its potential energy by a displacement x is given by

$$V = \frac{m}{2}(2\pi\nu_0)^2 x^2 , \tag{20.1}$$

where m is the mass and ν_0 the vibration frequency of the particle. The potential can be represented by a parabola in a xV-diagram. Both the potential and the restoring force tend to infinity with x and hence do not in a true sense represent a real field of force.

In older quantum theory one tried to improve the model by adding to the above potential higher powers of x as x^3, x^4, and so forth. This procedure may be useful when dealing with lower states. For higher states with larger vibration amplitudes the results thus obtained may sometimes be even more misleading than those obtained from the unmodified harmonic oscillator.

In wave mechanics, and occasionally in older quantum theory, potentials were introduced that fit much better with real molecular forces and are still simple enough to permit integration of the classical equations of motions or the Schrödinger wave equation.

In the theory of molecular vibrations we consider separately *polar* and *nonpolar* molecules. In polar molecules there is a Coulomb attraction extending with considerable magnitude to larger distances. The effect of the Coulomb force is to enable an infinite number of vibrational states to exist. On the other hand, nonpolar molecules with fairly short-range forces possess a fairly moderate number of states. These circumstances are illustrated in Fig. 2-11 which presents potentials of nonpolar and polar molecules, together with their vibrational levels in comparison with the simple harmonic oscillator. We may express the main features of molecular vibrational levels by saying that they are falling off in comparison to those of the harmonic oscillator. In polar molecules this depression of energy levels is sufficiently strong so as to allow for an infinite number of states below the dissociation energy D of the molecule.

The comparison of molecular vibrations is facilitated if in either case we choose for smaller vibrations the same frequency ν_0 as for the harmonic

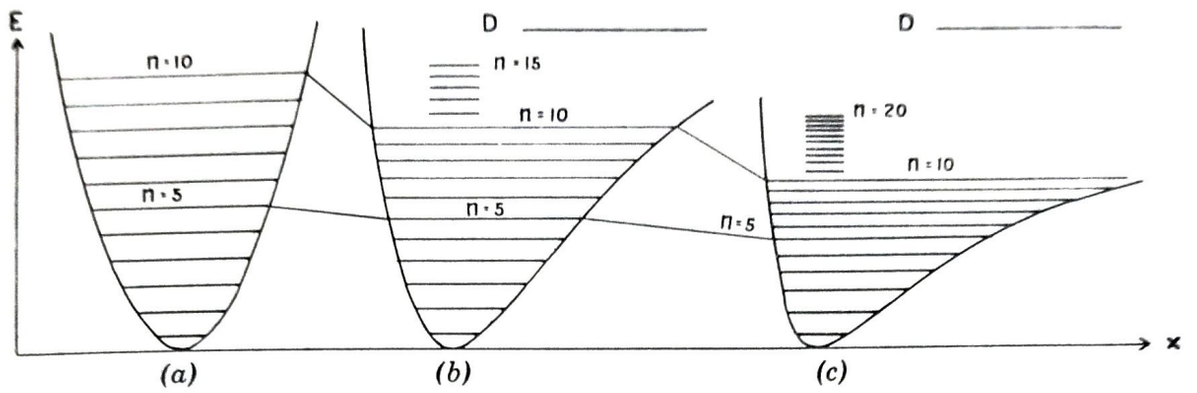

Fig. 2-11. (*a*) Harmonic oscillator; (*b*) nonpolar molecule; and (*c*) polar molecule.

oscillator. As a standard form for the nonpolar diatomic molecule of reduced mass $m = m_1m_2/(m_1 + m_2)$ we choose the Morse potential

$$V = \frac{m}{2}(2\pi\nu_0)^2a^2(1 - e^{-x/a})^2, \tag{20.2}$$

and for a polar molecule

$$V = \frac{m}{2}(2\pi\nu_0)^2a^2\frac{x^2}{(a + x)^2}. \tag{20.3}$$

As $x \to +\infty$ the two potentials approach the same limit, the dissociation energy of the molecule,

$$D = \frac{m}{2}(2\pi\nu_0)^2a^2. \tag{20.4}$$

The potentials may be written in the standard form

$$V = \frac{D\xi^2}{a^2}, \tag{20.5}$$

the definition thus being contained in the coordinate transformation $\xi = \xi(x)$. For the nonpolar molecule we put

$$\xi = a(1 - e^{-x/a}), \qquad x = a\log\frac{1}{1 - \xi/a}, \qquad \frac{dx}{d\xi} = \frac{1}{1 - \xi/a}, \tag{20.6}$$

the potential thus containing two arbitrary constants D and a. For the polar molecule we choose

$$\xi = \frac{ax}{a + x}, \qquad x = \frac{a\xi}{a - \xi}, \qquad \frac{dx}{d\xi} = \frac{1}{(1 - \xi/a)^2}. \tag{20.7}$$

In either case the energy equation is

$$\frac{p^2}{2m} + V = E, \tag{20.8}$$

and the linear momentum is given by

$$p = \pm\sqrt{2mD}\left(\frac{E}{D} - \frac{\xi^2}{a^2}\right)^{1/2} = \pm\frac{2D}{2\pi\nu_0 a}\left(\frac{E}{D} - \frac{\xi^2}{a^2}\right)^{1/2}. \tag{20.9}$$

Energy States of the Morse Potential Nonpolar Molecule

The simple potential (20.2) was never invented in older quantum theory. It was introduced in wave mechanics by P. M. Morse. Its application in older quantum theory is, however, still simpler than in wave mechanics. The energy states can be obtained from a single phase integral which according to (20.6) and (20.9), by appropriate choice of the sign of the integrand, is

$$J = \oint p\,dx = \pm\frac{2D}{2\pi\nu_0}\oint\left(\frac{E}{D} - \frac{\xi^2}{a^2}\right)^{1/2}\frac{d\xi}{\xi - a}. \tag{20.10}$$

The integral is most easily evaluated by complex integration which yields

$$J = \frac{2D}{\nu_0}\left[1 - \left(1 - \frac{E}{D}\right)^{1/2}\right]. \tag{20.11}$$

By $J = (n + \frac{1}{2})h$,

$$1 - \left(1 - \frac{E}{D}\right)^{1/2} = \frac{h\nu_0}{2D}\left(n + \frac{1}{2}\right), \tag{20.12}$$

or

$$E = h\nu_0\left(n + \frac{1}{2}\right) - \frac{[h\nu_0(n + \frac{1}{2})]^2}{4D}. \tag{20.13}$$

Equation 20.11 can also be used for computation of the vibration frequency ν for arbitrary amplitudes, yielding

$$\frac{1}{\nu} = \frac{dJ}{dE} = \frac{1}{\nu_0(1 - E/D)^{1/2}}, \qquad \nu = \nu_0\left(1 - \frac{E}{D}\right)^{1/2}. \tag{20.14}$$

By (20.11) the maximum value of the phase integral is $J = 2D/\nu_0$ for $E = D$. Hence for the highest state the quantum number n is given by

$$\frac{J}{h} = n + \frac{1}{2} \leqq \frac{2D}{h\nu_0}, \qquad E \approx D. \tag{20.15}$$

Energy States of Polar Molecules

For polar molecules (20.3) we similarly obtain by (20.7) and (20.9)

$$J = \frac{2D}{\nu_0}\cdot\frac{a}{2\pi}\oint\left(\frac{E}{D} - \frac{\xi^2}{a^2}\right)^{1/2}\frac{d\xi}{(\xi - a)^2} = \frac{2D}{\nu_0}\left(\frac{1}{(1 - E/D)^{1/2}} - 1\right). \tag{20.16}$$

This yields the following energy formula

$$\frac{1}{(1 - E/D)^{1/2}} - 1 = \frac{h\nu_0}{2D}\left(n + \frac{1}{2}\right) \tag{20.17}$$

or

$$E = \frac{h\nu_0(n + \frac{1}{2}) + [h\nu_0(n + \frac{1}{2})]^2/4D}{\left[1 + \frac{h\nu_0}{2D}(n + \frac{1}{2})\right]^2}. \tag{20.18}$$

By (20.16) the frequency is given by

$$\frac{1}{\nu} = \frac{dJ}{dE} = \frac{1}{\nu_0(1 - E/D)^{3/2}}, \qquad \nu = \nu_0\left(1 - \frac{E}{D}\right)^{3/2}. \tag{20.19}$$

Integration of the Equations of Motion for Molecular Potentials

Following the Hamilton-Jacobi method of integration, we introduce the auxiliary quantity

$$u_1 = 2\pi w_1 = 2\pi\nu t = 2\pi\nu\frac{\partial S}{\partial E}. \tag{20.20}$$

The action function S is given by integrals of a similar form as the definite integral for J in (20.10) and (20.16). Taking $x_{\max}$ for the fixed lower limit, we must choose the negative sign of the square root of the integrand. At the same time using the frequency equations (20.14) and (20.19), we obtain for the Morse potential

$$u_1 = -\left(1 - \frac{E}{D}\right)^{1/2}\int \frac{d\xi}{(E/D - \xi^2/a^2)^{1/2}(a - \xi)}, \tag{20.21}$$

and for the polar molecule

$$u_1 = -\left(1 - \frac{E}{D}\right)^{3/2}\int \frac{a\,d\xi}{(E/D - \xi^2/a^2)^{1/2}(a - \xi)^2}. \tag{20.22}$$

Integration of (20.21) yields

$$u_1 = \arccos\left(\frac{D}{E}\right)^{1/2}\left(\frac{1 - E/D}{1 - \xi/a} - 1\right), \tag{20.23}$$

$$\frac{1}{1 - \xi/a} = \frac{1 + (E/D)^{1/2}\cos u_1}{1 - E/D}, \tag{20.24}$$

$$a\log\frac{1}{1 - \xi/a} = x = a\log\frac{1 + (E/D)^{1/2}\cos u_1}{1 - E/D}. \tag{20.25}$$

The integration of (20.22) is considerably more difficult. In addition to u_1, which corresponds to the mean anomaly of the Kepler problem, we also

need an auxiliary quantity u corresponding to the eccentric anomaly. Returning to the original coordinate x, we have

$$u_1 = -\left(1 - \frac{E}{D}\right)^{3/2} \int \frac{(1 + x/a)\, d(x/a)}{[(E/D)(1 + x/a)^2 - (x/a)^2]^{1/2}}$$

$$= -\int \frac{\{1 + (1 - E/D)x/a - E/D\}\, d[(1 - E/D)x/a]}{\{E/D - [(1 - E/D)x/a - E/D]^2\}^{1/2}}. \tag{20.26}$$

Writing

$$\frac{(1 - E/D)\, x/a - E/D}{(E/D)^{1/2}} = \cos u, \tag{20.27}$$

or

$$\frac{x}{a} = \frac{E/D + (E/D)^{1/2} \cos u}{1 - E/D}, \tag{20.28}$$

we obtain

$$u_1 = u + \left(\frac{E}{D}\right)^{1/2} \sin u. \tag{20.29}$$

The quantity

$$\varepsilon = \left(\frac{E}{D}\right)^{1/2} \tag{20.30}$$

thus corresponds to the eccentricity of the elliptic orbit of the Kepler problem.

21. TRANSITION PROBABILITIES FOR ANHARMONIC OSCILLATORS

Fourier Coefficients for the Morse Potential

We now write (20.25) on the form

$$\frac{x}{a} = \log \frac{1 + \varepsilon \cos u_1}{1 - \varepsilon^2}, \qquad \varepsilon = \left(\frac{E}{D}\right)^{1/2}. \tag{21.1}$$

Expanding the right-hand side in a Fourier series,

$$\frac{x}{a} = \sum_{m=-\infty}^{\infty} \frac{x_m}{a} e^{imu_1}, \qquad x_{-m} = x_m, \tag{21.2}$$

we obtain by partial integration

$$\frac{x_m}{a} = \frac{1}{2\pi} \int_0^{2\pi} \frac{x}{a} e^{-imu_1}\, du_1 = \frac{1}{2\pi im} \int_0^{2\pi} \frac{e^{-imu_1}(-2 \sin u_1)\, du_1}{2/\varepsilon + 2 \cos u_1}$$

$$= \frac{1}{2\pi im} \oint \frac{(z - 1/z)\, dz}{z^m(z^2 + 1 + 2z/\varepsilon)}, \qquad z = e^{iu_1}. \tag{21.3}$$

For the path of integration in the complex z-plane we choose the unit circle. Apart from the point $z = 0$, the integrand has no other singularities than the simple poles in $z = z_1$ and $z = z_2$

$$z_1 = -\frac{1}{\varepsilon}[1 - (1 - \varepsilon^2)^{1/2}], \qquad z_2 = -\frac{1}{\varepsilon}[1 + (1 - \varepsilon^2)^{1/2}], \qquad z_1 z_2 = 1. \tag{21.4}$$

Deforming the path into a small circle around the pole $z = z_2$, we find the result:

$$\frac{x_m}{a} = -\frac{1}{m}\frac{z_2 - 1/z_2}{z_2^m(z_2 - z_1)} = \frac{(-1)^{m-1}}{m}\left(\frac{\varepsilon}{1 + (1 - \varepsilon^2)^{1/2}}\right)^m. \tag{21.5}$$

To compute x_0 we must proceed differently, writing

$$\begin{aligned}\frac{x_0}{a} &= \frac{1}{2\pi}\int_0^{2\pi} \log\frac{1 + \varepsilon\cos u_1}{1 - \varepsilon^2}\, du_1 \\ &= \frac{1}{2\pi i}\oint\left[\log\frac{(\varepsilon/2)(z - z_2)}{1 - \varepsilon^2} + \log\frac{z - z_1}{z}\right]\frac{dz}{z}.\end{aligned} \tag{21.6}$$

As can be seen by extending the circular path of integration toward infinity, there will be no contribution from the second term. Omitting this term and contracting the path of integration around $z = 0$, we obtain the result:

$$\frac{x_0}{a} = \log\frac{1 + (1 - \varepsilon^2)^{1/2}}{2(1 - \varepsilon^2)}. \tag{21.7}$$

For comparison we give the wave-mechanical matrix elements $x_{nn'}$, $n' > n$. (The computation cannot be given here.) We expect the difference $n' - n$ to correspond to the former m. In this way, when $n' \neq n$, (21.5) is replaced by

$$\frac{x_{nn'}}{a} = \frac{(-1)^{n'-n-1}}{n' - n}\cdot\frac{(\varepsilon_n\varepsilon_{n'})^{1/2}}{\varepsilon_{(n'+n)/2}}\cdot\frac{\varepsilon_{n+1/2}\varepsilon_{n+3/2}\cdots\varepsilon_{n'-1/2}}{[1 + (1 - \varepsilon_{n+1/2}^2)^{1/2}]\cdots[1 + (1 - \varepsilon_{n'-1/2}^2)^{1/2}]}. \tag{21.8}$$

In the case of $n' = n$ the corresponding expression is

$$\begin{aligned}\frac{x_{nn}}{a} &= \log\frac{4D}{h\nu_0} + \Psi\left(\frac{4D}{h\nu_0} - n - 1\right) \\ &\quad - \Psi\left(\frac{4D}{h\nu_0} - 2n - 1\right) - \Psi\left(\frac{4D}{h\nu_0} - 2n - 2\right),\end{aligned} \tag{21.9}$$

$\Psi(x) = \Pi'(x)/\Pi(x)$ being the logarithmic derivative of the factorial function. Apart from terms of the order of magnitude $(h\nu_0/2D)^2$ the expression (21.9)

may be replaced by

$$\frac{x_{nn}}{a} = \log \frac{1 - \frac{1}{2}(n + \frac{1}{2})h\nu_0/2D}{[1 - (n + \frac{1}{2})h\nu_0/2D]^2} = \log \frac{1 + (1 - \varepsilon_n^2)^{1/2}}{2(1 - \varepsilon_n^2)}, \tag{21.10}$$

and thus is in complete agreement with (21.7).

Fourier Coefficients of Polar Molecules

Consider the solution (20.28) for the polar molecule

$$\frac{x}{a} = \frac{\varepsilon^2 + \varepsilon \cos u}{1 - \varepsilon^2}, \qquad u_1 = u + \varepsilon \sin u. \tag{21.11}$$

Expanding the coordinate x in a Fourier series

$$x = \sum_m x_m e^{imu_1}, \qquad x_{-m} = x_m, \qquad \frac{x_m}{a} = \frac{1}{2\pi} \int_0^{2\pi} \frac{x}{a} e^{-imu_1} du_1, \tag{21.12}$$

we at once obtain for $m = 0$

$$\frac{x_0}{a} = \frac{3}{2} \frac{\varepsilon^2}{1 - \varepsilon^2}. \tag{21.13}$$

If $m = 0$, it is advisable first to perform an integration by parts and to substitute for u_1 according to (21.11). Then

$$\begin{aligned} \frac{x_m}{a} &= \frac{1}{2\pi m} \int_0^{2\pi} \exp(-imu - im\varepsilon \sin u)^{1/2} \, d\left(-\frac{ix}{a}\right) \\ &= \frac{1}{1 - \varepsilon^2} \cdot \frac{1}{2\pi m^2} \int_0^{2\pi} \exp(-imu - im\varepsilon \sin u)^{1/2} \cdot im\varepsilon \sin u \, du \\ &= \frac{(-1)^{m-1}}{1 - \varepsilon^2} \cdot \frac{\varepsilon}{2m} \cdot \sum_{k=0}^{\infty} \frac{(-1)^k (m + 2k)!}{k!\,(m + k)!} \left(\frac{m\varepsilon}{2}\right)^{m-1+2k}. \end{aligned} \tag{21.14}$$

The above series is a Bessel function which may be written as

$$\frac{x_m}{a} = \frac{(-1)^{m-1}}{1 - \varepsilon^2} \frac{\varepsilon}{m} J'_m(m\varepsilon). \tag{21.15}$$

Here also we offer for comparison the matrix element of wave mechanics. If $n' = n$,

$$\frac{x_{nn}}{a} = \frac{3}{2} \frac{\varepsilon_n^2}{1 - \varepsilon_n^2}, \qquad \varepsilon_n^2 = \frac{E_n}{D}. \tag{21.16}$$

If $n' \neq n$ the matrix elements are somewhat more difficult to obtain than the Morse potential matrix elements for nonpolar molecules. They can, however, be computed by ordinary methods of wave mechanics without too serious

difficulties. If written as a sum, they read

$$\frac{x_{nn'}}{a} = \left[1 - \left(\frac{n' - n}{2\rho + n' + n}\right)^2\right]^{\rho+2} \cdot \frac{(-1)^{n'-n-1}}{1 - \varepsilon^2} \cdot \frac{\varepsilon}{2(n' - n)} \cdot \sum_{k=0}^{n} \frac{(-1)^k (n' - n + 2k)!}{k!\,(n' - n + k)!} \left(\frac{n' - n}{2}\varepsilon\right)^{n'-n-1+2k} \cdot F_k, \quad (21.17)$$

where, for brevity, we have put

$$\rho(\rho - 1) = b^4, \qquad \varepsilon = \varepsilon_{(n'+n)/2},$$
$$F_k = f_{-(n'-n-1)} \cdots f_{-1} f_0 f_1^2 \cdots f_k^2, \quad (21.18)$$
$$f_k = \frac{1 - \varepsilon^2_{(n'-n-2+2k)/2}/\varepsilon_{(n'+n)/2}}{1 - \varepsilon^2_{(n'-n-2+2k)/2}}.$$

If $k = n + 1$, $f_{n+1} = 0$, and the series (21.17) terminates by $k = n$, F_k and f_k can be written differently but the above expression for $x_{nn'}$ appears to provide the best correspondence with x_m in (21.14).

22. SEMICLASSICAL TRANSITION PROBABILITIES IN HYDROGEN

A rigorous theory of absorption and emission processes can be given only on the basis of wave mechanics, using matrix elements, as will be dealt with in Chapter 4, Section 32. Notwithstanding, we can gain a fairly good insight into the true connection between the ideas of classical and quantum theory with respect to radiation processes by studying the Bohr electron orbits and their classical frequencies and Fourier components. Moreover the study of details in this older concept is not a failure even from a practical point of view. It affords a good orientation in the matter and frequently provides formulas that, although simpler, are actually not very different from those given by wave mechanics.

We start by trying to find selection rules for the *azimuthal* and *equatorial* (or *magnetic*) quantum numbers l and m as defined according to (18.5) by the quantized phase integrals

$$J_2 = (l + \tfrac{1}{2})h \qquad \text{and} \qquad J_3 = mh. \quad (22.1)$$

The corresponding frequencies (18.11) are $\nu_2 = 0$, $\nu_3 = 0$, since by (18.10) the electron energy in a purely Coulomb field depends on the main quantum number n, and hence on J_1 only. The orbital motion of the electron thus has a single main frequency ν_1 corresponding to radial oscillations. By deviations from the Coulomb field, which will always appear in polyelectron atoms, and by the presence of a magnetic field the frequencies ν_2 and ν_3 will be

different from zero. Correspondingly the angle variables

$$w_2 = \nu_2 t, \qquad w_3 = \nu_3 t, \tag{22.2}$$

are no more constants. By (19.11) and (19.14*b*) these variables (multiplied by 2π) have been identified with certain angles

$$u_2 = 2\pi w_2 = \psi_0 - (\kappa - 1) f(u_1), \qquad u_3 = 2\pi w_3 = \varphi_0, \tag{22.3}$$

ψ_0 giving the direction of the major elliptic axis and φ_0 the intersection of the orbital and the xy-coordinate planes. In order to see what can be inferred from the correspondence principle, we try to express electron coordinates by these angles. The angles φ_0, ψ_0, and a third angle α between the orbital and the xy-plane are shown in Fig. 2-8. We first express the Cartesian coordinates by ordinary spherical coordinates r, ϑ, φ,

$$x \pm iy = r \sin \vartheta e^{\pm i(\varphi - \varphi_0) \pm i\varphi_0}, \qquad z = r \cos \vartheta. \tag{22.4}$$

The multiplication factors or amplitudes of $e^{\pm i\varphi_0}$ and $e^0 = 1$, that is,

$$(x \pm iy)_m = r \sin \vartheta e^{\pm i(\varphi - \varphi_0)}, \qquad z_m = r \cos \vartheta, \tag{22.5}$$

are independent of φ_0. Hence the selection rules for the above combinations of coordinates must be

$$\Delta m = \pm 1, \qquad \Delta m = 0$$

or, in more detail,

$$m \to \pm 1 \quad \text{for } x \pm iy, \qquad m \to m \quad \text{for } z. \tag{22.6}$$

Writing (17.24) as

$$\begin{aligned} \cos \vartheta &= \sin \alpha \sin \psi, \\ \sin \vartheta \sin (\varphi - \varphi_0) &= \cos \alpha \sin \psi, \end{aligned} \tag{22.7}$$

and using in addition the equation

$$\sin \vartheta \cos (\varphi - \varphi_0) = \cos \psi, \tag{22.8}$$

which can easily be obtained from Fig. 2-8, we find that the expressions for the amplitudes (22.5) become

$$\begin{aligned} \left(\frac{x + iy}{r}\right)_m &= \sin \vartheta e^{i(\varphi - \varphi_0)} = \frac{1 + \cos \alpha}{2} e^{i\psi} + \frac{1 - \cos \alpha}{2} e^{-i\psi}, \\ \left(\frac{x - iy}{r}\right)_m &= \sin \vartheta e^{-i(\varphi - \varphi_0)} = \frac{1 - \cos \alpha}{2} e^{i\psi} + \frac{1 + \cos \alpha}{2} e^{-i\psi}, \\ \left(\frac{z}{r}\right)_m &= \cos \vartheta = \frac{\sin \alpha}{2i} (e^{i\psi} - e^{-i\psi}). \end{aligned} \tag{22.9}$$

Similarly, as has already been used above for $\varphi = (\varphi - \varphi_0) + \varphi_0$, we write $\psi = (\psi - u_2) + u_2$. The difference $\psi - u_2$ depends on r through $u_1 = 2\pi w_1$ in (17.33) but is independent of u_2. Hence the exponentials $e^{\pm i\psi_0}$ occur in all three of the above expressions. By the correspondence principle the selection rules for all coordinates must be

$$l \to l \pm 1. \tag{22.10}$$

The radiation intensity and absorption power connected with these transitions must be proportional to the square modulus of the corresponding amplitudes as, for instance, the amplitude

$$\tfrac{1}{2}(1 + \cos\alpha)e^{i(\psi-\psi_0)}$$

of $e^{i\psi_0} = e^{iu_2}$ in the first equation of (22.9).

The question now arises of how to account for the factors $e^{\pm i(\psi-\psi_0)}$ of these amplitudes that depend on r and $u_1 = 2\pi w_1$. They will affect the Fourier coefficients of the plane Cartesian coordinates $x' = r\cos(\psi - \psi_0)$ and $y' = r\sin(\psi - \psi_0)$ in the orbital plane, however not their square sum $r^2 = x'^2 + y'^2$. According to the classical theory the intensity of radiation is proportional to

$$\overline{x'^2 + y'^2} = \overline{r^2}. \tag{22.11}$$

Hence it appears reasonable to use only the Fourier expansion of r.

This agrees with the attitude of wave mechanics in simply disregarding phase factors of modulus 1 as $e^{\pm i(\psi-\psi_0)}$.

We now quite formally adopt the notations used in wave mechanics for matrix elements. Expressing the angle α by

$$\cos\alpha = \frac{m}{l + \frac{1}{2}}, \tag{22.12}$$

and using for l and m mean values of these quantum numbers for the upper and lower combining states, we may insist upon having arrived at approximate expressions of square "matrix elements" as follows:

$$\begin{aligned}
\left|\left(\frac{x + iy}{r}\right)^{m+1\,m}_{l+1\,l}\right|^2 &= \left(\frac{1 + \cos\alpha}{2}\right)^2 = \frac{(l + 1 + m + \frac{1}{2})^2}{(2l + 2)^2}, \\
\left|\left(\frac{x - iy}{r}\right)^{m-1\,m}_{l+1\,l}\right|^2 &= \left(\frac{1 - \cos\alpha}{2}\right)^2 = \frac{(l + 1 - m + \frac{1}{2})^2}{(2l + 2)^2}, \\
\left|\left(\frac{z}{r}\right)^{m\,m}_{l+1\,l}\right|^2 &= \left(\frac{\sin\alpha}{2}\right)^2 = \frac{(l + 1)^2 - m^2}{(2l + 2)^2},
\end{aligned} \tag{22.13a}$$

and

$$\left|\left(\frac{x-iy}{r}\right)^{m-1\,m}_{l-1\,l}\right|^2 = \left(\frac{1+\cos\alpha}{2}\right)^2 = \frac{(l+m-\frac{1}{2})^2}{(2l)^2},$$

$$\left|\left(\frac{x+iy}{r}\right)^{m+1\,m}_{l-1\,l}\right|^2 = \left(\frac{1-\cos\alpha}{2}\right)^2 = \frac{(l-m-\frac{1}{2})^2}{(2l)^2}, \qquad (22.13b)$$

$$\left|\left(\frac{z}{r}\right)^{m\,m}_{l-1\,l}\right|^2 = \left(\frac{\sin\alpha}{2}\right)^2 = \frac{l^2-m^2}{(2l)^2}.$$

These "matrix elements" are different from the true matrix elements of wave mechanics (31.42), (31.43), and (32.6) only in the following respect. In wave mechanics the denominators $(2l+2)^2$ and $(2l)^2$ are replaced by $(2l+2)^2-1$ and $(2l)^2-1$, and the nominators $(l+\frac{3}{2}\pm m)^2$ and $(l-\frac{1}{2}\pm m)^2$ by $(l+\frac{3}{2}\pm m)^2-\frac{1}{4}$ and $(l-\frac{1}{2}\pm m)^2-\frac{1}{4}$.

If in (22.13) we had used a common value of the inclination angle α, the square sum of the matrix elements would have been

$$\frac{1}{2}\left[\left(\frac{1+\cos\alpha}{2}\right)^2+\left(\frac{1-\cos\alpha}{2}\right)^2\right]+\left(\frac{\sin\alpha}{2}\right)^2=\frac{1}{2}. \qquad (22.14)$$

Since α is different for the three elements of (22.13*a*) and (22.13*b*), the sums also differ from $\frac{1}{2}$, namely,

$$\frac{(l+1)(2l+3)+\frac{1}{4}}{(2l+2)^2} \quad \text{for } l\to l+1, \qquad (22.15a)$$

$$\frac{l(2l-1)+\frac{1}{4}}{(2l)^2} \quad \text{for } l\to l-1. \qquad (22.15b)$$

Omitting $\frac{1}{4}$ in the nominators and changing the denominators as explained above, all of which makes little difference for larger l, we get the same result as in wave mechanics:

$$\frac{l+1}{2l+1} \quad \text{for } l\to l+1, \qquad (22.16a)$$

$$\frac{l}{2l+1} \quad \text{for } l\to l-1. \qquad (22.16b)$$

The sum of these expressions is 1, hence independent of l.

This may be taken as a proof that the total rate of radiation from an atom in a given state is proportional to the square of the Fourier coefficients in an expansion of r. The radiation energy produced by the electron is the same as though its motion were restricted to a given rigid orbital plane. By the above considerations it has been proved, however, that the radiant energy is equally divided on the various polarization components $m\to m+1$, $m\to m-1$,

and $m \to m$, and that it is relatively distributed in proportions

$$\frac{l+1}{2l+1} \quad \text{and} \quad \frac{l}{2l+1}$$

on the quantum transitions $l \to l+1$ and $l \to l-1$.

Radial Fourier Coefficients in Elliptic Motion

The calculation of radial Fourier coefficients for the Kepler problem is almost the same as that for polar molecules in the preceding section. We begin by writing (17.32) and (17.33) as

$$\begin{aligned} \frac{r}{a} &= 1 + \varepsilon \cos u. \\ 2\pi w_1 = u_1 &= u + \varepsilon \sin u, \\ du_1 &= (1 + \varepsilon \cos u)\, du, \end{aligned} \tag{22.17}$$

and putting

$$\begin{aligned} \frac{r}{a} &= \sum_{\nu=-\infty}^{+\infty} \left(\frac{r}{a}\right)_\nu e^{i\nu u_1}, \\ \left(\frac{r}{a}\right)_\nu &= \frac{1}{2\pi} \int_0^{2\pi} \frac{r}{a} \cdot e^{-i\nu u_1}\, du_1. \end{aligned} \tag{22.18}$$

The zero coefficient, $\nu = 0$, is simply the mean value of r/a, by (18.21)

$$\overline{\left(\frac{r}{a}\right)} = \left(\frac{r}{a}\right)_0 = 1 + \tfrac{1}{2}\varepsilon^2. \tag{22.19}$$

As an exception this result is different from that of wave mechanics which by (32.29) yields $-\frac{3}{2}\varepsilon$ for the corresponding matrix element. On the other hand, the quantity $-\frac{3}{2}\varepsilon$ equals the Fourier coefficient of the Cartesian coordinate

$$-\frac{x'}{a} = -(\varepsilon + \cos u). \tag{22.20}$$

The matrix element of wave mechanics thus in some sense represents a constant mean dipole moment of the electron orbit.

The remaining Fourier coefficients are computed as in (21.14) and (21.15). Using (22.17) and performing an integration by parts

$$\begin{aligned} \left(\frac{r}{a}\right)_\nu &= \frac{1}{2\pi} \frac{\varepsilon}{i\nu} \int_0^{2\pi} \exp\left(-i\nu u - i\nu\varepsilon \sin u\right)^{1/2} \sin u\, du \\ &= \frac{\varepsilon}{\nu} \frac{d}{d(\varepsilon\nu)} \frac{1}{2\pi} \int_0^{2\pi} \exp\left(-i\nu u - i\nu\varepsilon \sin u\right)^{1/2} du \\ &= \frac{\varepsilon}{\nu} J'_\nu(\varepsilon\nu). \end{aligned} \tag{22.21}$$

In this formula we replace $2a$ by the mean value of the elliptic major axis for n and n', b by the mean value of the minor axis, ν by $|n' - n|$, and ε by

$$\varepsilon = \frac{c}{a} = \left(1 - \frac{b^2}{a^2}\right)^{1/2} = \left[1 - (l+1)^2 \Big/ \left(\frac{n+n'}{2}\right)^2\right]^{1/2} \tag{22.22}$$

The above formula for $(r/a)_\nu$ is then the same as that for corresponding matrix elements obtained by wave mechanics (32.34).

The calculation of transition probabilities is an intricate problem both in older quantum theory and in wave mechanics. A clear insight into the possibilities of radiation of an atom in a given state is therefore not so easily obtained. The above considerations, which are based on the classical description of electronic orbits, may provide some useful additional illustrations of the radiation processes.

CHAPTER 3

The General Foundations of Wave Mechanics

23. LIGHT QUANTA AND MATTER WAVES

The Limitations of the Older Atomic Theory

In the preceding sections we have attempted to develop the atomic theory of Bohr as far as possible in different directions, and also introduced certain systematic improvements, such as half-integral quantization for librational motions. In this way we have displayed both the great power and the marked limitations of this theory.

First, the older quantum theory furnishes a correct picture and correct numerical results, both with respect to stationary eigenvalues and transition probabilities, for several simple one-particle systems, such as the harmonic oscillator and the simple rotator. These models do not represent any existing atom or molecule but appear as subproblems in the treatment of real atomic systems, in particular, molecules.

Further, Bohr's theory undoubtedly gives a fairly good qualitative description of atomic electron orbits and their arrangement into electron spheres, explaining both the characteristic X-ray spectra and the essential features of the periodic table of elements. Quantitatively, however, the theory breaks down completely as soon as it is applied to systems of more than one electron. The cause of this is, essentially, that it is impossible to formulate the general atomic problem consistently within the framework of the older quantum theory, with its subdivision of the problem into two parts: a mechanical part, concerned with the determination of classically possible electron orbits, and another part in which the stationary orbits are singled out by means of specific quantum conditions.

The only atomic systems that may be treated in a completely satisfactory way by the theory of Bohr are the hydrogen atom and the homologous ions He^{+}, Li^{++}, Be^{+++} with only one electron. Here spectroscopic measurements of

the energy levels match the theoretical predictions perfectly; and even transition probabilities may be deduced to a fair approximation by means of the correspondence principle. Moreover the normal Zeeman effect is easily explained; the anomalous Zeeman effect, however, requires the additional hypothesis of the rotating spinning electron. Another effect that may be treated fairly satisfactorily, but which has not been discussed in the preceding chapters, is the Stark effect, that is, the electric splitting of spectral lines.

Furthermore the theory may (for one-electron problems) partially explain the relativistic fine structure of spectral lines due to the variation of the electronic mass. This splitting is very small in the case of the hydrogen atom but increases for the higher ions which contain a greater nuclear charge. It also appears in the X-ray spectra as a very large separation of the energy terms; without the theory of relativity, therefore, one would not be able to understand the relationship between these terms.

In this way we may claim to have achieved a complete understanding of the relativistic fine structure of the energy levels for an atom or an ion with only one orbital electron. However, a closer investigation shows that the relativistic theory only predicts about half the number of terms which actually appear. This circumstance does not become evident for the hydrogen atom and corresponding ions, since the energy terms in this case coincide in pairs. On the other hand, the X-ray terms (and the optical terms of other atomic systems, such as the alkali atoms) are separate, so that the theory is clearly deficient.

We have already shown how the terms are doubled when the hypothesis of electronic spin is introduced. This, however, reveals yet another defect of the original theory for the relativistic fine structure, since the correct theoretical evaluation of the terms found experimentally rests on an erroneous quantization procedure: The phase integral J_2 in the theory of the Kepler problem is taken to be $(l + 1)h$ instead of $(l + \frac{1}{2})h$.

When all is said and done, however, the most weighty argument against the older quantum theory is its complete failure to account for problems involving two or more electrons.

Formally this weakness undoubtedly stems from the fact that the problem (as already mentioned) is formulated in two steps, one mechanical and one quantum-theoretic. Hence we shall now attempt to show how one has developed a new and better formulation by means of the so-called wave mechanics, which makes no explicit appeal to mechanics in the usual sense nor to specific quantum conditions.

Quantum Theory and the Hypothesis of Light Quanta

Let us recapitulate briefly some basic notions of quantum theory. The quantum of action was first discovered during the theoretical treatment of a

statistical problem, namely, the energy distribution of blackbody thermal radiation. The crucial assumption of Max Planck was that the phase cells in coordinate-momentum space had a finite extension

$$\Delta q \, \Delta p = h, \tag{23.1}$$

where h is the smallest unit of the dynamical quantity which we call *action*. Applying this equation to a monochromatically oscillating system, such as the harmonic oscillator, and observing that energy and time are canonically conjugate dynamical quantities, we find that

$$\Delta E \cdot T = h, \tag{23.2}$$

or

$$\Delta E = h\nu, \tag{23.3}$$

where ν is the proper frequency of the oscillator, since $T = 1/\nu$ is then the temporal extension of the phase cell.

Here right away we have a quantization of the harmonic oscillator with any two successive levels separated by the constant energy quantum $h\nu$. This means that such an oscillator may only absorb or emit radiant energy in such finite quanta. Since, moreover, the frequency of the absorbed or emitted radiation must accord with the frequency of the oscillator, we are very close to the notion of light quanta.

This conclusion was not, however, drawn by Planck himself but (somewhat later) by Einstein, during his investigation of the photoelectric effect. This hypothesis, written as

$$E = h\nu, \tag{23.4}$$

and (23.1) together constitute the essential basis of the entire quantum theory. It is clear that Bohr's law of frequencies

$$E_1 - E_2 = h\nu \tag{23.5}$$

is a consequence of this notion of light quanta and the energy principle. A light quantum is indivisible and must be absorbed as a whole by the atom, with a corresponding increase of the energy of the latter; conversely it may only be emitted as a whole, with a corresponding decrease of the atomic energy.

Bohr's quantum conditions are closely connected with (23.1). The simple result that the energy intervals of a harmonically oscillating system are all equal (to the oscillator frequency multiplied by h) is, of course, not very helpful if the frequency of the oscillating system considered is not fixed but depends on the orbital extensions. It is, however, easily seen that an equivalent condition may be laid down,

$$\oint p \, dq = nh, \tag{23.6}$$

where n is an integer, or at least $\Delta n = 1$. This equation expresses the assertion that the area enclosed by the "orbit" of a point in the two-dimensional phase space is equal to an integral number of action quanta h. This, of course, corresponds to the fact that the phase space is partitioned into cells having the extension h. Equation (23.6) was the equation introduced by Niels Bohr into atomic theory in order to quantize the electronic orbits.

De Broglie's Hypothesis of "Matter Waves"

According to electrodynamic theory, electromagnetic radiation possesses an energy E and a momentum

$$p = \frac{E}{c}. \tag{23.7}$$

This means that a light quantum $E = h\nu$ must have the momentum

$$p = \frac{h\nu}{c} = \frac{h}{\lambda}, \tag{23.8}$$

where ν is the frequency, and λ the wavelength of the light; this may be written as

$$\lambda = \frac{h}{p}. \tag{23.9}$$

Briefly, (23.9) may be said to constitute the basis for de Broglie's hypothesis of "matter waves," and also the subsequent wave mechanics of Schrödinger. We assume that just as the photon has the character of a wave, appearing as interference phenomena, so material particles must also have a wave character which correspondingly ought to appear under special circumstances, such as in the stationary states of atoms.

It is immediately evident that this hypothesis may serve to explain the quantum conditions for stationary electronic orbits in an atom. Let us imagine that an electron moves along a circular orbit with the radius r. If the "matter waves" are to create standing waves, their wavelengths must be expressible as

$$\lambda = \frac{2\pi r}{n}, \tag{23.10}$$

where n is an integer; substitution of this in (23.9) then leads to

$$pr = n\frac{h}{2\pi}, \tag{23.11}$$

that is, the well-known result that the angular momentum of the electron is an integral multiple of $h/2\pi$.

If the interference equation for an electronic orbit is written

$$\oint \frac{dq}{\lambda} = n, \tag{23.12}$$

and multiplied by h, we arrive at the quantum condition

$$\oint p\, dq = nh. \tag{23.13}$$

Actually de Broglie's investigations of the "matter waves" were conducted along lines differing somewhat from those indicated here. The original point of departure was the relativistic consideration of a stationary oscillation process in a coordinate system x_0, y_0, z_0, t_0,

$$\psi = A(x_0, y_0, z_0) \sin 2\pi\nu_0 t_0. \tag{23.14}$$

If the system moves with a velocity v relative to another coordinate system x, y, z, t, the oscillation process will take the form

$$\psi = A\left(\frac{x - vt}{(1 - v^2/c^2)^{1/2}}, y, z\right) \sin 2\pi\nu_0 \frac{t - vx/c^2}{(1 - v^2/c^2)^{1/2}} \tag{23.15}$$

in the latter system, by the relativistic transformations; in other words, it will describe a wave. This wave possesses two different velocities, the group velocity

$$u_g = v \tag{23.16}$$

which is the velocity of the amplitude crest, and the *phase velocity*

$$u = \frac{c^2}{v}, \tag{23.17}$$

that is, the propagation velocity of the elementary waves through the so-called wave packet. The latter is only an apparent velocity which in this case is evident from the fact that it is greater than that of light.

Let us now assume, formally, that (23.14) represents a particle with the energy

$$E_0 = h\nu_0 = m_0c^2. \tag{23.18}$$

In the "fixed" coordinate system the oscillation process has the frequency

$$\nu = \frac{\nu_0}{(1 - v^2/c^2)^{1/2}}, \tag{23.19}$$

and the energy of the particle in this system is

$$E = \frac{m_0c^2}{(1 - v^2/c^2)^{1/2}} = h\nu. \tag{23.20}$$

Hence the equation $E = h\nu$ is invariant.

The wavelength is easily found from (23.15) to be

$$\lambda = \frac{c^2(1 - v^2/c^2)^{1/2}}{vv_0} = \frac{h(1 - v^2/c^2)^{1/2}}{m_0 v} = \frac{h}{p}. \tag{23.21}$$

We shall now show that if we ascribe such matter waves to a particle with the velocity v, then the group velocity of these waves will be v. The general connection between group and phase velocities is easily found in the following way. Adding two monochromatic waves of the form

$$\exp\left[2\pi i\nu\left(t - \frac{x}{u}\right)\right]^{1/2}$$

but with slightly different frequencies and velocities, it is immediately evident that

$$u_g = \frac{d\nu}{d(\nu/u)}. \tag{23.22}$$

We now multiply both the numerator and the denominator of (23.22) by h, and observe that

$$u = \nu\lambda = \frac{\nu h}{p} = \frac{E}{p}; \tag{23.23}$$

hence we must have

$$u_g = \frac{dE}{dp}. \tag{23.24}$$

On the other hand, it follows from Hamilton's equations that

$$v = \frac{dE}{dp}, \tag{23.25}$$

an expression that is easily verified for both in the nonrelativistic and relativistic cases.

$$\begin{aligned} E &= \frac{p^2}{2m} + V, & \frac{dE}{dp} &= \frac{p}{m} = v, \\ E &= c(p^2 + m_0^2c^2)^{1/2} + V, & \frac{dE}{dp} &= \frac{cp}{(p^2 + m_0^2c^2)^{1/2}} = v. \end{aligned} \tag{23.26}$$

Thus the group velocity is, in general, equal to the particle velocity

$$u_g = v. \tag{23.27}$$

24. THE SCHRÖDINGER EQUATIONS

The Amplitude Equation for Matter Waves

It is clear that our primitive considerations of the phase matching of the matter waves along an imagined particle trajectory have only a heuristic

value. We must assume that these "matter waves," if they are to constitute standing waves of some kind in an atom in a stationary state, must be waves in space and not one-dimensional waves along a trajectory. Moreover we must expect that they correspond to waves in an inhomogeneous medium; hence the only sensible way to proceed is to attempt to formulate the wave equation describing their propagation.

If we consider a system with the energy E, it is reasonable (since $E = h\nu$) to assume that the corresponding matter waves are monochromatic, so that it is sufficient to find the differential equation determining the amplitude. If the particle moves in a force field with the potential energy $V(x, y, z)$, we have

$$\frac{p^2}{2m} + V = E \tag{24.1}$$

or

$$p^2 = 2m(E - V),$$

$$\frac{1}{\lambda} = \frac{p}{h} = \frac{1}{h}[2m(E - V)]^{1/2}. \tag{24.2}$$

Thus our conjecture that the "medium" of propagation for these "waves" is inhomogeneous holds true, since the wavelength depends on the positional coordinates x, y, z through V.

For a plane wave

$$\psi = \exp\left[\frac{2\pi i}{\lambda}(s_x x + s_y y + s_z z)\right]^{1/2}, \tag{24.3}$$

$$s_x^2 + s_y^2 + s_z^2 = 1$$

we have

$$\nabla^2\psi + \left(\frac{2\pi}{\lambda}\right)^2\psi = 0, \tag{24.4}$$

as is easily verified. We now assume that there exists a wave amplitude function, or briefly wave function, $\psi = \psi(x, y, z)$ which describes the state of the system in some way or other; furthermore the equation for this amplitude is taken to have the form (24.4), even for a variable wavelength λ. It then follows from (24.2) that the equation must be

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0. \tag{24.5}$$

This is the so-called Schrödinger wave equation for a single particle.

The General Formulation of the Wave Equation

Dividing by $8\pi^2 m/h^2$, it takes the form

$$\left[\frac{1}{2m_0}\left(\frac{h}{2\pi i}\right)^2\nabla^2 + V\right]\psi = E\psi \tag{24.6}$$

which has a close formal resemblance to the energy equation

$$H = \frac{1}{2m_0} p^2 + V = E. \tag{24.7}$$

It is easily seen that an exact analogy may be obtained by regarding all mechanical quantities as operators, acting on the wave function ψ. Ordinary numerical quantities such as E, and likewise all functions of the coordinates such as $V(x, y, z)$, are taken to act as multipliers; momenta, on the other hand, must be replaced by differential operators. Substituting

$$p_x = \frac{h}{2\pi i} \frac{\partial}{\partial x}, \qquad \text{etc.} \tag{24.8}$$

in (24.6), we may write this equation as

$$H\psi = E\psi. \tag{24.9}$$

The amplitude equation may consequently be regarded as an equation determining the quantized energy values. As we shall see later it is possible to formulate other equations, similar to (24.9), which determine the quantized values of other dynamical variables.

The first important result of the application of the wave equation (24.5) to atomic problems was the deduction of the quantized energy values for the hydrogen atom with $V = -e^2/r$. In this case it turned out that the solutions of the equation were, in general, singular for $r = 0$ or $r = \infty$. Only for certain specific values of the energy E was it possible to obtain solutions having finite values in these two points; these solutions are then finite and uniquely determined everywhere. The specific energy values corresponding to such solutions turned out to be the well-known stationary energy levels of the hydrogen atom.

Even though we have as yet said nothing about the physical interpretation of the wave function, it thus seems very natural to introduce as a general requirement that it be uniquely given and finite in the whole coordinate space. We must assume that the various dynamic variables, or their mean values, are to be determinable by means of the wave function; in order for such a determination to be at all possible this function must necessarily have these properties.

However, the wave equation (24.5) has been (tentatively) deduced only for a single particle, with three degrees of freedom. The question now is how to extend this equation to be valid for other problems, involving less or more degrees of freedom: for instance, a system of several individual particles.

In this connection it should be noted that the wave equation (24.9) is not to be regarded as deduced from fundamental principles, and thus valid a priori; rather it represents a guess as to a possible way to describe atomic

systems. Its validity can only be verified or falsified by an experimental observation of its predictions, such as the energy levels of atoms.

Proceeding as before, it is now important that the three-dimensional wave equation (24.9) have a form that may be readily generalized to hold for any system of particles interacting by means of conservative forces. As soon as the Hamiltonian of the system is found we may formulate a wave equation of the same form as (24.9), writing all components of momentum in the Hamiltonian as differential operators

$$p_{x_1} = \frac{h}{2\pi i}\frac{\partial}{\partial x_1}, \qquad \text{etc.} \tag{24.10}$$

Since the kinetic energy in the Hamiltonian is a quadratic function of the momenta, this will always lead to an energy equation in the form of a second-order partial differential equation, that is, a wave equation. However, the wave function is now dependent on the coordinates of all the particles, that is, on $3n$ variables, if n is the number of particles. In other words, the equation represents waves, not in ordinary three-dimensional space but in an abstract higher-dimensional mathematical space.

The main result of these considerations is that (24.9) constitutes a consistent formulation of the quantum-theoretical energy problem; whether it is correct or not is a matter of experimental verification. Before proceeding, however, we shall discuss certain aspects of this formulation of the problem.

Let us assume that the plane wave (24.3) represents a particle moving with a given constant velocity and the momentum

$$p = \frac{h}{\lambda}, \tag{24.11}$$

so that

$$p_x = ps_x, \qquad p_y = ps_y, \qquad p_z = ps_z, \tag{24.12}$$

where s_x, s_y, s_z are the direction cosines of the direction of wave propagation. We may then write

$$\psi = \exp\left[\frac{2\pi i}{h}(p_x x + p_y y + p_z z)\right]; \tag{24.13}$$

hence it follows that, for a free particle with a given velocity, an application of the differential operators

$$\frac{h}{2\pi i}\frac{\partial}{\partial x}, \qquad \text{etc.}$$

is equivalent to a multiplication by the constant value of the corresponding component of momentum. We must assume that a similar procedure may be adopted even if the momenta are no longer constant. In particular, if we

consider the energy function, a quadratic function of the momentum component plus a potential function, when acting on the wave function, is equivalent to the multiplication by a number, that is, an energy value.

However, one thing must be kept in mind when dynamical variables are replaced by operators, that the latter do not always commute. We have, for instance, that

$$\frac{\partial}{\partial x} x\psi = x\frac{\partial \psi}{\partial x} + \psi,$$

$$x\frac{\partial}{\partial x}\psi = x\frac{\partial \psi}{\partial x},$$

or

$$\left(\frac{\partial}{\partial x} x - x\frac{\partial}{\partial x}\right)\psi = \psi. \tag{24.14}$$

Hence

$$(p_x x - x p_x)\psi = \frac{h}{2\pi i}\psi \tag{24.15}$$

which may be written as a pure operator relation,

$$p_x x - x p_x = \frac{h}{2\pi i}. \tag{24.16}$$

Generally one may show, similarly to (24.14), that

$$q_i q_j - q_j q_i = 0, \qquad p_i p_j - p_j p_i = 0,$$

$$p_j q_i - q_i p_j = \frac{h}{2\pi i}\delta_{ij}. \tag{24.17}$$

Thus coordinates and momenta are mutually commutative but a coordinate does not commute with its canonically conjugate mementum; this applies both for Cartesian and for general coordinates.

This must be taken into account when a wave equation is to be determined. In curvilinear coordinates the kinetic energy depends both on the coordinates and the momenta. Hence if the wave equation is to be formulated in a unique way by means of the corresponding Hamiltonian, we must know beforehand the order in which the coordinates and momenta appear in each term. The safest procedure is to start off with the wave equation in Cartesian coordinates, where the kinetic energy is a quadratic function of the momenta alone and thus independent of the coordinates.

Orthogonality of the Eigenfunctions

The solutions ψ_n corresponding to the eigenvalues E_n for the energy, or to eigenvalues for other dynamical variables, are called *eigenfunctions*. These

functions have the very important and interesting property of mutual orthogonality, just like the amplitude functions of a vibrating string.

In order right away to obtain as general results as possible we note the following: An eigenfunction ψ_n, being the solution of a linear homogeneous differential equation, contains an arbitrary (and in general, complex) numerical factor; the complex conjugate function ψ_n^* will then also be a solution of this equation. There would be no necessity to consider complex functions, if it were possible to make all wave functions real. Actually this is often done in the mathematical treatment of waves, but then only for purposes of simplification. Not so in wave mechanics: For certain quantized eigenvalues of dynamical variables the two real functions ψ_1 and ψ_2 in $\psi = \psi_1 + i\psi_2$ are different, so that we may not write $\psi = (a + ib)\psi_R$; furthermore they must both be employed in the calculation of physical quantities. Hence we shall, from the start, consider complex eigenfunctions, even though these in certain simple cases will turn out to be real.

Let us first consider eigenfunctions for the energy. If ψ_n is such a function for the eigenvalue E_n, we have

$$H\psi_n = E_n\psi_n. \tag{24.18}$$

Multiplying by another eigenfunction ψ_m and integrating over the whole coordinate space, we obtain

$$E_n \int \psi_m \psi_n \, d\tau = \int \psi_m H \psi_n \, d\tau, \tag{24.19}$$

where $d\tau$ is the element of volume in coordinate space: $d\tau = dx\, dy\, dz$ for a single particle, or $d\tau = dx_1\, dy_1\, dz_1\, dx_2\, dy_2\, dz_2$ for two particles.

Similarly we find

$$E_m \int \psi_n \psi_m \, d\tau = \int \psi_n H \psi_m \, d\tau \tag{24.20}$$

or

$$(E_n - E_m) \int \psi_m \psi_n \, d\tau = \int (\psi_m H \psi_n - \psi_n H \psi_m) \, d\tau. \tag{24.21}$$

The right-hand side of (24.21) is always zero as a consequence of the character of the energy operator. For consider the identity

$$\psi_m \nabla^2 \psi_n - \psi_n \nabla^2 \psi_m = \operatorname{div} (\psi_m \nabla \psi_n - \psi_n \nabla \psi_m). \tag{24.22}$$

Assuming that ψ is regular in $r = 0$ and applying the Gauss theorem to (24.22), we obtain

$$\int (\psi_m \nabla^2 \psi_n - \psi_n \nabla^2 \psi_m) \, d\tau = \int \left(\psi_m \frac{\partial \psi_n}{\partial r} - \psi_n \frac{\partial \psi_m}{\partial r} \right) dS, \tag{24.23}$$

where dS is the surface element of a sphere with the radius r containing the region of integration. If ψ_n decreases at least as rapidly as r^{-1} when $r \to \infty$, the right-hand side of (24.23) will go to zero; consequently, since ∇^2 is the only operator in H that is important in this connection, the right-hand side of (24.21) will vanish. Thus we have

$$(E_n - E_m)\int \psi_m \psi_n \, d\tau = 0 \tag{24.24}$$

or

$$\int \psi_m \psi_n \, d\tau = 0, \qquad E_m \neq E_n. \tag{24.25}$$

If no eigenvalues coincide, this may be written

$$\int \psi_m \psi_n \, d\tau = 0, \qquad m \neq n. \tag{24.26}$$

A coincidence of eigenvalues means that there correspond two or more linearly independent solutions to a given eigenvalue E_n; this will, for instance, be the case for the hydrogen atom. However, it is possible to generate a corresponding number of mutually orthogonal linear combinations of these solutions, so that (24.26) may be taken to hold generally.

The same relations also hold for eigenfunctions of other dynamical variables, since it turns out that an operator F (depending on coordinates and momenta) which represents a real dynamical variable will have the same properties as those found for the energy function, that is,

$$\int (\psi_m F \psi_n - \psi_n F \psi_m) \, d\tau = 0, \qquad m \neq n. \tag{24.27}$$

Hence it is possible to determine states that are simultaneously quantized with respect to several dynamical variables; the maximum number of such possibilities of quantization is equal to the number of degrees of freedom of the system. For a particle motion in a central field, for instance, we may quantize the energy, components of angular momentum such as

$$m_z = xp_y - yp_x, \tag{24.28}$$

and the square of the angular momentum vector

$$\mathbf{m}^2 = m_x^2 + m_y^2 + m_z^2. \tag{24.29}$$

The quantized values of these are [compare (29.19)]

$$\begin{aligned} \mathbf{m}^2 &= \left(\frac{h}{2\pi}\right)^2 l(l+1), \qquad l = 0, 1, \cdots, \\ m_z &= \frac{h}{2\pi} m, \qquad\qquad m = -l, \cdots, 0, \cdots, l. \end{aligned} \tag{24.30}$$

If we have determined the quantized states for such a complete set of dynamical variables—or, as one may also put it, the simultaneous eigenfunctions for these variables—there is no longer any possibility of coinciding eigenvalues within this set; hence we may, in this case, always write

$$\int \psi_{n'l'm'}\psi_{nlm}\, d\tau = 0, \qquad n', l', m' \neq n, l, m. \tag{24.31}$$

Eigenvalues and Eigenfunctions for the Harmonic Oscillator

In order to illustrate what we have just said about eigenvalues and eigenfunctions, we shall now deduce the quantized eigenvalues for the harmonic oscillator; these, as we have stated above, will turn out to be

$$E_n = (n + \tfrac{1}{2})h\nu_0, \qquad n = 0, 1, \cdots, \tag{24.32}$$

by the laws of wave mechanics, in contrast to the values $E_n = nh\nu_0$ of the older quantum theory. (The term ν_0 is the mechanical proper frequency of the oscillator.) Denoting the linear deflection of the oscillator by x and the corresponding momentum by $p_x = m\dot{x}$, we may write the Hamiltonian of the system,

$$H = \frac{1}{2m}\, p_x{}^2 + \frac{m}{2}(2\pi\nu_0)^2x^2. \tag{24.33}$$

Hence the one-dimensional wave equation is

$$\left\{\frac{d^2}{dx^2} + \frac{8\pi^2m}{h^2}\left[E - \frac{m}{2}(2\pi\nu_0)^2x^2\right]\right\}\psi = 0. \tag{24.34}$$

It is now convenient to introduce the coordinate transformation

$$x = \frac{1}{2\pi}\left(\frac{h}{m\nu_0}\right)^{1/2}\xi. \tag{24.35}$$

so that (24.34) takes the simplified form

$$\left(\frac{d^2}{d\xi^2} + \frac{2E}{h\nu_0} - \xi^2\right)\psi = 0, \tag{24.36}$$

All solutions of this equation are regular, except at infinity, $\xi = \infty$; here we shall have the asymptotic solutions

$$\psi = \exp\,(\pm\tfrac{1}{2}\xi^2)^{1/2}, \tag{24.37}$$

where only the minus sign is acceptable.

In general an equation of this kind may be simplified by separating off such asymptotic factors, by writing, say,

$$\psi = \exp\,(\pm\tfrac{1}{2}\xi^2)^{1/2}y, \tag{24.38}$$

so that the following equation for y ensues:

$$\left(\frac{d^2}{d\xi^2} - 2\xi\frac{d}{d\xi} + \frac{2E}{h\nu_0} - 1\right)y = 0. \tag{24.39}$$

This equation possesses two linearly independent solutions

$$\begin{aligned} y_0 &= c_0 + c_2\xi^2 + c_4\xi^4 + \cdots, \\ y_1 &= c_1 + c_3\xi^3 + c_5\xi^5 + \cdots. \end{aligned} \tag{24.40}$$

Both will in general approach e^{ξ^2} asymptotically when $\xi \to \infty$; the only exception to this occurs when one of the series (24.40) terminates, that is, is a polynomial of, say, degree n. This will also be the highest power when the polynomial is substituted in (24.39), and the corresponding coefficient turns out to be

$$-2n + \frac{2E}{h\nu_0} - 1 = 0. \tag{24.41}$$

Hence we obtain the eigenvalues

$$E_n = (n + \tfrac{1}{2})h\nu_0, \tag{24.42}$$

as already stated in (24.32).

The solutions of (24.39) may be written

$$y_n = H_n(\xi) = (-1)^n e^{\xi^2}\frac{d^n}{d\xi^n}e^{-\xi^2}, \tag{24.43}$$

where $H_n(\xi)$, $n = 0, 1, 2, \cdots$, are the so-called Hermite polynomials,

$$H_0 = 1, \qquad H_1 = 2\xi, \qquad H_2 = 4\xi^2 - 2, \cdots. \tag{24.44}$$

It is easily shown that these satisfy the equation

$$\left(\frac{d^2}{d\xi^2} - 2\xi\frac{d}{d\xi} + 2n\right)H_n(\xi) = 0. \tag{24.45}$$

We may write

$$u = e^{-\xi^2} \tag{24.46}$$

and differentiate $n + 2$ times to obtain

$$\begin{aligned} u' + 2\xi u &= 0, \\ &\vdots \\ u^{(n+2)} + 2\xi u^{(n+1)} + (2n + 2)u^{(n)} &= 0; \end{aligned} \tag{24.47}$$

using

$$u^{(n)} = (-1)^n e^{-\xi^2}H_n(\xi), \tag{24.48}$$

we then easily arrive from (24.47) to (24.45).

It is evident from the definition (24.43) of the Hermite polynomials that the latter may also be defined by a generating function

$$\psi(\xi, s) = e^{\xi^2} \cdot e^{-(\xi-s)^2} = e^{2\xi s - s^2} = \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} s^n. \tag{24.49}$$

This is easily verified by differentiating (24.49) n times with respect to s, and then putting $s = 0$.

This definition is particularly useful in the calculation of several definite integrals. We find, for instance, that

$$\int_{-\infty}^{\infty} e^{-\xi^2} \psi(\xi, s)\psi(\xi, t)\, d\xi = e^{2st} \int_{-\infty}^{\infty} e^{-(\xi-s-t)^2}\, d\xi$$

$$= \sqrt{\pi}\, e^{2st} = \sqrt{\pi} \sum_{n=0}^{\infty} \frac{2^n}{n!} s^n t^n. \tag{24.50}$$

On the other hand, this integral is also by (24.49) equal to

$$\sum_{n,\, n'=0}^{\infty} \frac{1}{n!\, n'!} s^n t^{n'} \int_{-\infty}^{\infty} e^{-\xi^2} H_n(\xi) H_{n'}(\xi)\, d\xi.$$

Hence it follows, firstly that

$$\int_{-\infty}^{\infty} e^{-\xi^2} H_n(\xi) H_{n'}(\xi)\, d\xi = 0, \qquad n' \neq n, \tag{24.51}$$

that is, the eigenfunctions for the oscillator are orthogonal; secondly, we find the integral of normalization

$$\int_{-\infty}^{\infty} e^{-\xi^2} H_n^2(\xi)\, d\xi = 2^n n! \sqrt{\pi} = N_n. \tag{24.52}$$

From the equation

$$\int_{-\infty}^{\infty} e^{-\xi^2} \psi(\xi, s)\psi(\xi, t)\xi\, d\xi = \sqrt{\pi}\, e^{2st}(s + t) = \sqrt{\pi} \sum_{n=0}^{\infty} \frac{2^n}{n!} (s^{n+1}t^n + s^n t^{n+1}), \tag{24.53}$$

we find, similarly, that

$$\xi_{nn+1} = \frac{1}{(N_n N_{n+1})^{1/2}} \int_{-\infty}^{\infty} e^{-\xi^2} H_n(\xi) H_{n+1}(\xi)\xi\, d\xi = \left[\frac{1}{2}(n + 1)\right]^{1/2}, \tag{24.54}$$

while all other such product integrals vanish.

The mutually orthogonal and normalized (more briefly, *orthonormal*) eigenfunctions for the oscillator may now be written

$$\psi_n(x) = \left[\frac{2\pi}{N_n}\left(\frac{mv_0}{h}\right)^{1/2}\right]^{1/2} e^{-\xi^2/2} H_n(\xi), \qquad \xi = 2\pi\left(\frac{mv_0}{h}\right)^{1/2} x. \tag{24.55}$$

It then follows from (24.54) that the matrix elements, which will later turn out to be of such a fundamental importance in the new quantum theory, may be written

$$x_{nn+1} = \int_{-\infty}^{\infty} \psi_n(x)\psi_{n+1}(x)x\,dx = \frac{1}{2\pi}\left(\frac{h}{mv_0}\right)^{1/2}\xi_{nn+1} = \left[\frac{(n+1)h}{8\pi^2 mv_0}\right]^{1/2} \tag{24.56}$$

in accordance with (17.12). All other matrix elements $x_{nn'}$ are zero, which means (as previously noted) that only the quantum transitions $n \to n+1$ and $n \to n-1$ occur in the harmonic oscillator, that is, by emission and absorption.

25. THE TIME-DEPENDENT WAVE EQUATION

Elimination of the Energy Parameter in Schrödinger's Equations

The amplitude equation discussed in the preceding section cannot be the general fundamental equation of quantum mechanics, since it contains a state variable, the energy E. Hence we must try to determine a time-dependent wave equation by eliminating this parameter.

In the general canonical transformations E and t, energy and time, appear as canonically conjugate quantities. The relations,

$$\begin{aligned} \dot{E} &= \frac{dH}{dt} = \frac{\partial H}{\partial t}, \\ \dot{q} &= \frac{\partial H}{\partial p}, \qquad \dot{p} = -\frac{\partial H}{\partial q}, \end{aligned} \tag{25.1}$$

indicate that E may be regarded as a coordinate with t as the corresponding momentum, or as a momentum with $(-t)$ as the corresponding canonically conjugate coordinate. Both of these points of view lead by our previously established rules to the same commutation relation for E and t, and the same differential operator for E, namely,

$$Et - tE = -\frac{h}{2\pi i}, \qquad E = -\frac{h}{2\pi i}\frac{\partial}{\partial t}. \tag{25.2}$$

This argument is, of course, somewhat incomplete. We may resort to the more general theory of canonical transformations, where a generalized action function $W = S - Et$ is introduced as a solution of the equation

$$H\left(q, \frac{\partial W}{\partial q}\right) + \frac{\partial W}{\partial t} = 0,$$

and write Hamilton's equations as $\dot{q} = \partial\bar{H}/\partial p$, $\dot{p} = -(\partial\bar{H}/\partial q)$, by means of the generalized Hamiltonian

$$H = \bar{H}(q, p, \tau) - E, \qquad \tau = t, \tag{25.3}$$

where E and τ are to be regarded as a set of new variables. This leads to

$$\dot{E} = \frac{\partial H}{\partial \tau} = \frac{\partial \bar{H}}{\partial \tau}, \qquad \dot{\tau} = 1 = -\frac{\partial \bar{H}}{\partial E}. \tag{25.4}$$

This furnishes a complete analogy and a sufficient justification of (25.2). For a given energy $E = h\nu$, the complete wave function will therefore contain a time factor

$$\exp\left[-\frac{2\pi i}{h}Et\right] = \exp\left(-2\pi i\nu t\right)^{1/2}.$$

A plane wave for a free particle with the components of momentum p_x, p_y, p_z, for instance, will then appear as a propagating wave

$$\psi = \exp\left[\frac{2\pi i}{h}(p_x x + p_y y + p_z z - Et)\right] \tag{25.5}$$

in the direction of the particle motion. It is evident from this that, once we have chosen the plus sign for the momentum operators

$$p_x = \frac{h}{2\pi i}\frac{\partial}{\partial x},$$

we must choose the minus sign for the energy operator E as in (25.2) and (25.3).

By these considerations, the general time-dependent wave equation must read

$$Hu = -\frac{h}{2\pi i}\frac{\partial u}{\partial t}. \tag{25.6}$$

For a system with a constant energy we may put

$$u = \exp\left[-\frac{2\pi i}{h}Et\right]\psi, \tag{25.7}$$

thus obtaining the amplitude equation

$$H\psi = E\psi \tag{25.8}$$

previously discussed.

The eigenfunctions for the energy may also be expressed by means of such time-dependent wave functions u, in the form

$$u_n = \psi_n \exp\left[-\frac{2\pi i}{h}E_n t\right]. \tag{25.9}$$

Complex Conjugate Eigenfunctions

The functions (25.7) and (25.9) are not the only ones that may be used to describe the state of a quantum-mechanical system; the complex conjugate functions u^* and u_n^* will do just as well. The latter would have resulted from the other possible choice of energy and momentum operators,

$$p_x = -\frac{h}{2\pi i}\frac{\partial}{\partial x}, \qquad E = \frac{h}{2\pi i}\frac{\partial}{\partial t}. \tag{25.10}$$

The differential equation for the complex conjugate wave function u^* must therefore read

$$Hu^* = \frac{h}{2\pi i}\frac{\partial u^*}{\partial t}. \tag{25.11}$$

In the further development of wave mechanics there is no longer any question of which of the two alternatives u and u^* to choose; it turns out that we need both of them. This is evident from the fact that one, both in the physical interpretation of formal wave-mechanical results and in the calculation of several physical quantities, makes use of the square of the modulus of the wave function u,

$$|u|^2 = u^*u. \tag{25.12}$$

The time-dependent eigenfunctions u_n in (25.9) are always complex quantities, and the position-dependent functions ψ_n may also (as already noted) be complex. When several states have coincident energy values, as in the hydrogen atom, the eigenfunctions ψ_n may be complex; this will, for instance, be the case if we want the component m_z of the angular momentum to have a given value, as shown in (24.28), (24.29), and (24.30).

As soon as the energy levels are split—say, by an external field of force—the eigenfunctions for each level once again become unique; the character of the force field then determines whether these functions are to be complex or real. If the Hamiltonian due to this external field contains first powers of the components of momentum, the corresponding eigenfunction will be complex. This is the case for a magnetic splitting of the energy levels, since a magnetic field H along the z-axis will give rise to a term

$$\frac{eH}{2m_0c}m_z, \qquad m_z = xp_y - yp_x \tag{25.13}$$

in the energy function. The correct formulation of the complex conjugate wave equation is thus

$$H^*u^* = \frac{h}{2\pi i}\frac{\partial u^*}{\partial t} \tag{25.14}$$

when $H^* \neq H$. The operator H^* is obtained by replacing all momenta p in the Hamiltonian by

$$-\frac{h}{2\pi i}\frac{\partial}{\partial q}.$$

We have already mentioned the fact that the eigenfunctions of any real dynamic variable F, that is, a real function of the coordinates and momenta, are orthogonal. From

$$\begin{aligned} F\psi_n &= F_n\psi_n, \\ F^*\psi^*_{n'} &= F_{n'}\psi^*_{n'} \end{aligned} \tag{25.15}$$

we obtain, in the usual way,

$$(F_n - F_{n'})\int \psi^*_{n'}\psi_n \, d\tau = \int (\psi^*_{n'}F\psi_n - \psi_n F^*\psi^*_{n'}) \, d\tau. \tag{25.16}$$

The orthogonality relations will then read

$$\int \psi^*_{n'}\psi_n \, d\tau = 0, \qquad F_{n'} \neq F_n, \tag{25.17}$$

provided that the integral on the right-hand side of (25.16) always vanishes.

As an example we shall show that this is the case if F is taken to be the operator m_z in (24.28), which we shall write as

$$\begin{aligned} m_z &= \frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right), \\ m_z^* &= -\frac{h}{2\pi i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \end{aligned} \tag{25.18}$$

Integrating in parts, we find that

$$\begin{aligned} \frac{h}{2\pi i}\int \left(\psi^*_{n'}x\frac{\partial\psi_n}{\partial y} + \psi_n x\frac{\partial\psi^*_{n'}}{\partial y}\right) d\tau = 0, \\ \frac{h}{2\pi i}\int \left(\psi^*_{n'}y\frac{\partial\psi_n}{\partial x} + \psi_n y\frac{\partial\psi_{n'}}{\partial x}\right) d\tau = 0, \end{aligned} \tag{25.19}$$

provided that the eigenfunctions vanish sufficiently rapidly toward the limits of integration $-\infty < x, y, z < +\infty$. Subtraction then yields

$$\int (\psi^*_{n'}m_z\psi_n - \psi_n m_z^*\psi^*_{n'}) \, d\tau = 0. \tag{25.20}$$

Thus we have demonstrated the general validity of the orthogonality relations (25.17) for dynamic variables that are linear (for example, the components of angular momentum) or quadratic (the energy) functions of the momenta.

It may be shown that this validity also holds if the dynamic variables are third- or fourth-degree, or even arbitrary, functions of the momenta. For arbitrary functions of both the coordinates and momenta, however, the order of the latter in products is of some importance, so that these functions must have a certain specific (self-adjoint) character if the above assertion is to hold.

Since all eigenvalue equations are linear, an eigenfunction will be indeterminate with respect to the absolute modulus. It is, however, practical to use so-called normalized eigenfunctions; the obvious procedure is then to put the integral of the squared modulus of the eigenfunction $|\psi_n|^2 = \psi_n^* \psi_n$ equal to unity. Thus we supplement the orthogonality relations (25.17) and write

$$\int \psi_{n'}^* \psi_n \, dt = \delta_{nn'}. \tag{25.21}$$

The eigenfunctions ψ_n then constitute a so-called orthonormal system which will (in general) also be complete in the coordinate region considered. By "complete" we mean that an almost (that is, except for certain limitations) completely arbitrary function ψ in this region may be expressed by a linear combination of these eigenfunctions ψ_n.

For the time-dependent energy eigenfunctions u_n in (25.9) it is easily seen that the same relations

$$\int u_{n'}^* u_n \, d\tau = \delta_{nn'}, \tag{25.22}$$

hold; that is, the functions u_n also constitute an orthonormal system.

The Quantum-Mechanical Principle of Superposition

The general solution of the time-dependent wave equation (25.6) may now be written

$$u = \sum_n c_n u_n, \tag{25.23}$$

where the c_n are constant coefficients. This is the quantum-mechanical principle of superposition which corresponds mathematically to the classical principle of superposition for waves or oscillations in a continuous medium, for example, standing waves in a vibrating string.

This principle introduces something quite novel into our treatment of atomic systems, and therefore deserves a close examination. As yet we know nothing about the eigenfunctions, except that they describe a state with a given energy E_n for the system considered. Equation 25.23 then seems to indicate that states of the system exist for which the energy has several different values, which apparently contradicts the energy law.

We should not let this confuse us, nor allow it to pass without a more detailed examination, but rather attempt immediately to find a sensible interpretation of this equation.

Energy values may be determined by measurements of frequencies; this is the procedure actually adopted in atomic physics, where the energy levels of atoms are found by means of the observed spectral lines. Frequencies may, in turn, be measured by counting the number of oscillations N within a given interval of time Δt,

$$\nu = \frac{N}{\Delta t}, \tag{25.24}$$

The number N, however, is always subject to an uncertainty ΔN, which may in principle be as large as unity. Allowing for other inaccuracies of measurement, we may put $\Delta N \geqq 1$, or

$$\Delta\nu \, \Delta t \geqq 1. \tag{25.25}$$

Exactly the same sort of thing happens if we try to express a periodic function within an interval Δt by means of a Fourier integral. Fourier analysis does not recognize this wave train as monochromatic but represents it as a group of waves with a certain "spread" $\Delta\nu$ in the frequency ν, of the order indicated by (25.25).

A function defined by, say, $f(t) = \exp(2\pi i\nu_0 t)$ in the interval $-T/2 \leqq t \leqq T/2$, and by $f(t) = 0$ outside this interval, is resolved by Fourier analysis into

$$\begin{aligned} f(t) &= \int_{-\infty}^{\infty} g(\nu) \exp(2\pi i\nu t)\, d\nu, \\ g(\nu) &= \frac{\sin \pi(\nu - \nu_0)T}{\pi(\nu - \nu_0)}. \end{aligned} \tag{25.26}$$

Clearly the frequencies are spread over all possible values, but with a strong maximum at $\nu = \nu_0$. Hence, taking the mean interval of uncertainty to lie within the first zero of $g(\nu)$, we obtain

$$(\nu - \nu_0)T = 1 \qquad \text{or} \qquad \Delta\nu = \frac{1}{T}; \tag{25.27}$$

the corresponding uncertainty relation for physical measurements is then

$$\Delta\nu \geqq \frac{1}{T} \qquad \text{or} \qquad \Delta\nu \, \Delta t \geqq 1 \tag{25.28}$$

as in (25.25).

Applying (25.25) to energy measurements and putting $E = h\nu$, we find

$$\Delta E \, \Delta t \geqq h, \tag{25.29}$$

This is a particular version of the quantum-mechanical uncertainty relation for two canonically conjugate quantities q and p,

$$\Delta q \, \Delta p \geqq h,$$

proposed by Heisenberg. It expresses the assumption that a coordinate and its corresponding momentum may not be simultaneously measured with arbitrarily great accuracy; on the contrary, the product of their individual uncertainties must always be at least as large as the quantum of action.

The most lucid way of illustrating the quantum-mechanical principle of superposition is perhaps to consider the stream of photons in a light ray. Assuming the radiation to be homogeneous and monochromatic, that is, to have a constant frequency and direction of propagation, we need only one more quantity in order to describe the state of the photons completely: the polarization. For polarized light this may be given by the angle between the direction of polarization and a fixed x-axis normal to the direction of propagation z; the polarization directions x and y are then characterized by the angles $\varphi = 0°$ and $\varphi = 90°$.

Consider now the meaning of the statement that the photons in the ray are in the state of polarization $\varphi = \alpha$. If a polariscope is inserted in the direction α, it will then let all the photons pass through unhindered; the same thing will happen if several polariscopes are placed one after the other along the ray in the same direction α. If, on the other hand, the radiation was unpolarized originally, the first polariscope would only let half the photons through, and these are then all in the state of polarization $\varphi = \alpha$ or ψ_α. Hence we see that this state is cultivated, so to speak, by the measuring apparatus, the polariscope in this case. When we speak of a given state of polarization, this always means that one has produced this state by means of some interference or other—that is, in principle, a measuring process; the simplest model of this process is then the polariscope inserted into the path of the light ray.

Imagine now that the next polariscope is inserted, first in the principal direction $\varphi = 0°$, and then in the principal direction $\varphi = 90°$. In the first case, a fraction $\cos^2 \alpha$ of the radiation will pass through the instrument; these photons are then all in the state $\psi_1 = \psi_{0°}$, since insertion of successive polariscopes in the direction $\varphi = 0°$ will let them all through unhindered. When the instrument is placed in the principal direction $\varphi = 90°$, it will let the rest of the photons (a fraction $\sin^2 \alpha$) through, and these will then all be in the state $\psi_2 = \psi_{90°}$, that is, polarized in the direction $\varphi = 90°$.

All this follows very naturally from the wave theory, expressing only the fact that the unit vector in the direction α may be resolved into its components along the x- and y-axis,

$$\mathbf{i}_\alpha = \mathbf{i} \cos \alpha + \mathbf{j} \sin \alpha, \tag{25.30}$$

and that the energy (the number of photons) is proportional to the amplitude squared,

$$|\mathbf{i}_\alpha|^2 = |\mathbf{i}|^2 \cos^2 \alpha + |\mathbf{j}|^2 \sin^2 \alpha = \cos^2 \alpha + \sin^2 \alpha = 1. \tag{25.31}$$

The situation is different, however, once we recognize the photons as independent individuals. We have seen that all the photons are originally in the uniquely defined state ψ_α. After a batch of photons has passed a polariscope in the direction $\varphi = 0°$, some of them (the fraction $\sin^2 \alpha$) have been eliminated, while the rest (the fraction $\cos^2 \alpha$) are all in the same uniquely defined state ψ_1. Similarly the fraction $\sin^2 \alpha$ will be in the state ψ_2 after having passed a polariscope in the direction $\varphi = 90°$.

All this may be expressed formally by the equation

$$\psi_\alpha = \psi_1 \cos \alpha + \psi_2 \sin \alpha. \tag{25.32}$$

The problem is: How is this equation to be interpreted? We may say that the states ψ_1 and ψ_2 are "potentially present" in the ratio $\cos^2 \alpha : \sin^2 \alpha$ but this can not mean that a certain number of photons are in the state ψ_1 and the rest in the state ψ_2, since such an assumption could not explain why all the photons are able to pass through the polariscope in the direction α.

The only logically tenable position is therefore to assume that *each photon* is in the state of polarization ψ_α. The expansion coefficients $\cos \alpha$ and $\sin \alpha$ in the compound state (25.30) thus only have a significance with respect to the successively performed measuring process that has been assumed. They may be used to express the probability that the photons (which of them, we do not know) pass over into one of the two states ψ_1 or ψ_2 under certain specific external influences. However, these probabilities are not given by the coefficients (amplitudes) $\cos \alpha$ and $\sin \alpha$ themselves but by their squares; quantities such as these coefficients are therefore often referred to as *probability amplitudes*.

We now return to (25.23). The individual states u_n are characterized by the assumption that the energy of the system in such a state may be thought of as measured, and found to equal E_n. However, a state may also be defined in other ways, that is, by measurement of other dynamic variables. Let us take the system to be a free electron and assume that this electron is known to be within a given region of volume $\Delta x\, \Delta y\, \Delta z$ in a given time interval Δt. We then know that it is impossible to define the momenta p_x, and so forth, or the energy, sharply; actually performed measurements would give differing results.

Once this is understood, we see how the expression (25.23) still can make some sense. The functions u_n signify that a measurement of the energy of the system would yield one of the values E_n as a result. Hence we may obtain different results of measurement for identical systems in the same state (25.23); for a large number of such measurements the values E_n will then appear with certain relative frequencies, resulting in a determinate mean value for the energy.

This mean value, and these frequencies (or probabilities) of obtaining

any particular result of a measurement, must be assumed to have some connection with the expansion coefficients c_n. In order to clarify the significance of these coefficients it has proved convenient to normalize the arbitrary wave function u, by putting

$$\int u^* u \, d\tau = 1. \tag{25.33}$$

Using the orthonormalization condition (25.22), we then find that

$$\sum_n c_n^* c_n = \sum_n |c_n|^2 = 1. \tag{25.34}$$

if we now choose to interpret (25.23) in such a way that each energy state u_n is present with a certain weight, the only sensible procedure seems to be that of putting this weight equal to $|C_n|^2$; this means, then, that the observational result $E = E_n$ will actually appear with this relative frequency. The mean value of a large number of energy measurements must then be

$$\bar{E} = \sum_n |c_n|^2 E_n. \tag{25.35}$$

This corresponds to the fact that the mean value for the energy may be calculated as follows:

$$\bar{E} = \int u^* H u \, d\tau = \sum_n c_n E_n \int u^* u_n \, d\tau = \sum_n c_n^* c_n E_n. \tag{25.36}$$

26. THE STATISTICAL INTERPRETATION OF WAVE MECHANICS

The Wave-Mechanical Calculation of Mean Values

Once we accept the fact that measurements of a dynamic variable for a quantum-mechanical system in a given state may yield different results, we are forced to assume that the majority of wave-mechanical physical predictions must be of a statistical nature. As a rule we will only be able to calculate mean values for a large number of measurements performed on identical systems in the same state; consequently a major question is whether wave mechanics is able to determine such mean values in a unique way.

Here, as previously, we have to propose (tentatively) some hypothesis, and then see if it leads to significant and useful results. It seems natural to attempt a generalization of (25.36) which (by assumption) determines the mean value for the energy.

So we consider a given state u and some dynamical variable F for a system; the latter is assumed to be measured a number of times, sufficient to determine its mean value $\bar{F}$. We now propose the hypothesis that this mean value

is determined wave-mechanically by the equation

$$\bar{F} = \int u^* F u \, d\tau. \tag{26.1}$$

Since $\bar{F}$ is real, this equation implies that the operator F has the form of a real quantity which will not be the case if it contains odd powers of the momenta, for example, of the angular momenta $m_z = xp_y - yp_x$, and so forth. Hence, to be on the safe side, we supplement the definition (26.1) with

$$\bar{F} = Re \int u^* F u \, d\tau = \tfrac{1}{2} \int (u^* F u + u F^* u^*) \, d\tau. \tag{26.2}$$

At this stage we shall content ourselves with noting that if u is an eigenfunction of F, the mean value of F will be the eigenvalue for this state, since this is the only possible result of measurement in this case. For, using

$$F u_n = F_n u_n, \tag{26.3}$$

it follows from (26.1) that

$$\bar{F} = \int u_n^* F u_n \, d\tau = F_n \int u_n^* u_n \, d\tau = F_n. \tag{26.4}$$

The Dipole Matrix and Bohr's Frequency Condition

This hypothesis concerning the mean value of a dynamic quantity also furnishes us with the possibility of ascertaining whether a given quantum-mechanical system is able to emit energy in the form of electromagnetic radiation. This depends essentially on whether the system may be said to have an oscillating electric dipole moment. Let us consider one single electron in an atom with the coordinates x, y, z and instantaneous dipole moments ex, ey, ez in the directions of the three axes. We now calculate the mean value of ex and find by (25.9), (25.23), and (26.1):

$$\overline{ex} = e \int u^* x u \, d\tau = \sum_{nn'} c_{n'}^* c_n e x_{n'n} \exp\left[\frac{2\pi i}{h} (E_{n'} - E_n) t\right], \tag{26.5}$$

$$x_{n'n} = \int \psi_{n'}^* x \psi_n \, d\tau, \tag{26.6}$$

where the $x_{n'n}$ are the elements of a so-called coordinate matrix, and $ex_{n'n}$ those of the corresponding dipole matrix.

The main thing to note in (26.5) is that it contains time-dependent harmonic factors with the oscillatory frequencies

$$\nu_{n'n} = \frac{E_{n'} - E_n}{h}. \tag{26.7}$$

Assuming that these mean values of the components of the dipole moments make the radiation of electromagnetic energy possible, analogous to the classical radiation from a dipole, we find that the dipoles of (26.5) will give rise to an emission of radiation with the frequencies (26.7). This is identical with the frequency law of Bohr in the older quantum theory; we obtain the same frequencies, and no more, as those predicted by the latter. This clearly furnishes a very strong support for our hypotheses.

We shall defer the detailed treatment of the matrix elements $x_{n'n}$ until later; at this point, we only note that they must, in some way or other, determine the transition probability between the states n' and n (or, if we like, the intensity of emitted radiation for the quantum transition between the two states). Actually it seems very natural to let these matrix elements replace the Fourier components in the classical solution of the corresponding problem. In this case the intensities and transition probabilities must be proportional to $e^2 |x_{nn'}|^2$, that is, to the squared modulus of the matrix element. It turns out that the correct value for the intensity of emission of light polarized in the x-direction, from an atom in the state n', is

$$I_{n'nx} = \frac{64\pi^4 \nu_{n'n}^4}{3c^3} e^2 |x_{n'n}|^2 \tag{26.8}$$

for the quantum transition $n' \to n$. This corresponds to the intensity of emission from a linear harmonic oscillator with the charge e, frequency $\nu_{n'n}$, and amplitude $2|x_{n'n}|$ in the x-direction. If we consider the classical Fourier analysis of the system,

$$x = \sum_{m=-\infty}^{\infty} x_m e^{2\pi i \nu_m t}, \qquad x_{-m} = x_m^*, \qquad \nu_m = m\nu_0, \tag{26.9}$$

where ν_0 is the classical fundamental frequency, we may obtain (26.8) from the formula for the intensity of the $(n' - n)$th overtone, substituting $\nu_{n'n}$ and $x_{n'n}$ for ν_m and x_m.

However, (26.5) does not furnish a completely satisfactory justification for our argument, since it contains the expansion coefficients c_n and $c_{n'}$ for the two corresponding states. By classical analogy, then, (26.5) would imply that the factors $|c_n|^2$ and $|c_{n'}|^2$ also appear in the radiation formula (26.8). This is true, to a certain extent, since the intensity of emission must be proportional to $|c_{n'}|^2$ if the latter is interpreted as the probability that a large number of identical systems be in the state n'. Similarly the absorption of radiation must be proportional to $|c_n|^2$. However, the simultaneous proportionality of the radiation intensity to both $|c_n|^2$ and $|c_{n'}|^2$ does not fit into the picture, and we shall therefore give a more complete justification for (26.8) later. This will be done by considering the interaction of the system with a radiation field, that is, by calculation of the coefficient of absorption corresponding to the

transition $n \to n'$. Utilizing the connection between the Einstein coefficients of probability, which we found during our discussion of Einstein's deduction of Planck's radiation law, we shall then arrive at (26.8). However, a direct deduction of this formula requires a quantization of the electromagnetic radiation field, using the methods of the so-called quantum electrodynamics, and will therefore not be attempted here.

Nevertheless it may be of some interest at this stage to show that the matrix elements may be defined in a way differing from (26.5), so that the general expansion coefficients c_n for an arbitrary state do not confuse the issue unnecessarily. We have made the reasonable assumption that the functions constitute a complete system in the coordinate region considered, so that—subject to certain restrictions—any function, and thus also $x\psi_n$, may be expanded in terms of these. Hence we may write

$$x\psi_n = \sum_{n'} \psi_{n'} x_{n'n}, \tag{26.10}$$

where

$$x_{n'n} = \int \psi_{n'}^* x \psi_n \, dt \tag{26.11}$$

due to the orthonormalization relations (25.21). These expansion coefficients $x_{n'n}$ are thus identical with our previously defined matrix elements.

Multiplying (26.10) by

$$\exp\left(-\frac{2\pi i}{h} E_n t\right),$$

we may write (26.10) and (26.11) as

$$\begin{aligned} xu_n &= \sum_n u_{n'} \exp(2\pi i \nu_{n'n} t) x_{n'n}, \\ \exp(2\pi i \nu_{n'n} t) x_{n'n} &= \int u_{n'}^* x u_n \, dt, \\ \nu_{n'n} &= \frac{1}{h}(E_{n'} - E_n). \end{aligned} \tag{26.12}$$

The expansion coefficients

$$x_{n'n} \qquad \text{or} \qquad \exp(2\pi i \nu_{n'n} t) x_{n'n}$$

may be arranged in a matrix, with the indices n and n' denoting rows and columns in the usual way; hence the name "matrix elements." It was on such matrices that Heisenberg based his first formulation of quantum mechanics, the so-called *matrix mechanics*.

The matrix elements always refer, as we have seen, to two states; and in the form (26.12), they may be said to contain a harmonic time factor

$\exp(2\pi i\nu_{n'n}t)$, with the same frequency $\nu_{n'n}$ as that we obtain by combining the two quantum states n' and n. In this, where no other expansion coefficients c_n or $c_{n'}$ appear, it is thus natural to accept the matrix elements as direct quantum-mechanical analogues to the classical Fourier coefficients.

Interpretation of the Wave Function as a "Probability Amplitude"

Our definition of quantum-mechanical mean values in general, and of coordinate mean values in particular, is compatible with the following hypothesis: The quantity $u^*u\,d\tau$ denotes the probability that the coordinates of the system be within an infinitesimal element of volume $d\tau$. Applied to an electron moving in the field of an atomic nucleus or ion, this means that the said quantity denotes the probability of finding the electron in the element of volume $dx\,dy\,dz$; it is then, of course, assumed that u is a wave function in the three-dimensional coordinate space of the electron. If u is a wave function for all the electrons in the atom, the probability of finding a single electron in a given element of volume must be formulated somewhat differently; however, such details need not concern us here.

First of all, we note that the above hypothesis is consistent. Since

$$\int u^*u\,d\tau = 1, \tag{26.13}$$

the sum of all probabilities is unity. Applied to one electron, this means that there is a complete certainty (that is, a probability equal to unity) of finding the electron somewhere in the space considered.

Evidently it is not the wave function itself, but the quantity $|u|^2 = u^*u$, that expresses the probability. The wave function, being a solution of a homogeneous linear differential equation, may (even after normalization) contain an arbitrary complex factor of modulus unity, that is, of the form $e^{i\delta}$, where δ is an arbitrary phase. In the product u^*u this phase factor is eliminated; consequently, it has no significance for the above definition of probabilities and for statistical computations of mean values.

Due to the analogy with classical-mechanical oscillating systems, where it is quite often the square of the amplitude (and not the amplitude itself) which is of importance, the wave function u has received the designation of *probability amplitude*. The reason for this does not, of course, lie only in this analogy. Actually the Schrödinger wave function—which, for one thing, is always connected with definite energy states for a system—is only a special case of the more general concept of a quantum-mechanical probability amplitude. At the present stage, however, we shall not pursue such general considerations.

The Charge and Current Density

The quantity u^*u may by the preceding considerations be thought of as a probability density or particle density. A more illustrative picture is perhaps obtained by introducing, for the motion of a single particle in the three-dimensional coordinate space, the quantity

$$\rho = eu^*u, \tag{26.14}$$

where e is the charge of the particle; this quantity may then be regarded as a charge density. Similarly we might introduce the mass density mu^*u for a particle with the mass m, and so on.

This charge density ρ is, of course, of a statistical nature. In general it will be subject to fluctuations; the latter must then by the law of conservation of electric charge be compensated by correspondingly statistical charge currents. A correct expression for these currents may be found in two ways. We might use the equation of continuity for electric charge to deduce the current density. However, we shall prefer to propose an expression for the current based on a somewhat intuitive application of the general procedure previously considered. The usefulness of this expression may then be checked subsequently, by means of the equation of continuity.

Our first task will then be to replace the velocity of the electron by a suitable operator, and the most natural choice seems to be

$$\dot{x} = \frac{1}{m} p_x = \frac{h}{2\pi i m} \frac{\partial}{\partial x}. \tag{26.15}$$

Here, however, we meet a difficulty already mentioned in connection with (26.2), that the operator (26.15) is complex. In analogy with (26.2), we therefore express the current vector $\mathbf{j}$ as follows:

$$\mathbf{j} = Re \frac{e}{m} \frac{h}{2\pi i} u^* \nabla u = \frac{eh}{4\pi i m} (u^* \nabla u - u \nabla u^*). \tag{26.16}$$

We now check that the equation of continuity

$$\operatorname{div} \mathbf{j} + \frac{\partial \rho}{\partial t} = 0 \tag{26.17}$$

is satisfied. By means of the wave equations (25.6) and (25.11) for u and u^*, we find

$$\operatorname{div} \mathbf{j} = \frac{eh}{4\pi i m} (u^* \nabla^2 u - u \nabla^2 u^*) = -e\left(u^* \frac{\partial u}{\partial t} + u \frac{\partial u^*}{\partial t}\right) = -\frac{\partial \rho}{\partial t}. \tag{26.18}$$

It is, however, to be noted that (26.15) does not represent the most general

definition of velocity; this is, in general, given by Hamilton's equation

$$\dot{x} = \frac{\partial H}{\partial p_x}. \tag{26.19}$$

For electromagnetic fields, where $\mathbf{p}^2$ in the Hamiltonian is to be replaced by $(\mathbf{p} + e/c\ \mathbf{A})^2$, this leads to

$$\dot{x} = \frac{1}{m}\left(p_x + \frac{e}{c} A_x\right). \tag{26.20}$$

Thus, allowing for the vector potential, the complete current vector becomes

$$\mathbf{j} = \frac{eh}{4\pi i m}(u^* \nabla u - u \nabla u^*) + \frac{e^2}{mc} \mathbf{A} u^* u. \tag{26.21}$$

The continuity equation (26.17) is satisfied also by this current vector, together with $\rho = eu^*u$.

Altogether, then, we have demonstrated that not only the continuity equation for electric charge, but also other continuity equations (such as, for instance, for mass), maintain their validity in the wave-mechanical statistical description of atomic systems.

27. SIMULTANEOUS EIGENVALUES AND EIGENFUNCTIONS FOR DYNAMIC VARIABLES

Quantum-Mechanical Constants of Motion

In the classical treatment of the problem of motion for an n-dimensional system, by means of the Hamilton-Jacobi differential equation, a primary task was to determine a complete set of so-called constants of the motion $a_1, a_2, \cdots, a_n$, or $E, a_2, \cdots a_n$, where E is the energy. We shall now discuss the quantum-mechanical counterpart to these constants of motion.

In wave mechanics dynamical variables are represented by operators F. That such a quantity be constant during the motion would be expressed classically by the equation

$$\dot{F} = 0. \tag{27.1}$$

As yet, we have no idea how the operator $\dot{F}$ is to be defined in wave mechanics. The only definition of operators which, at this stage, would lead to a satisfactory definition of F seems to be that used in the matrix representation (26.10) to (26.12) of the coordinate x. Defining the matrix elements of an ordinary operator F by

$$Fu_n = \sum_{n'} F_{n'n} u_{n'}, \tag{27.2}$$

that is, by means of the time-dependent energy eigenfunctions u_n, instead of

[as in (26.10)] the amplitude functions ψ_n, we find that these matrix elements

$$F_{n'n} = \int u_{n'} F u_n \, d\tau \tag{27.3}$$

will then, by (26.12), contain the time-dependent factor

$$\exp(2\pi i \nu_{n'n} t) = \exp\left[\frac{2\pi i}{h}(E_{n'} - E_n)t\right]. \tag{27.4}$$

Hence there is a possibility of defining the operator $\dot{F}$ by

$$\dot{F}u_n = \sum_{n'} u_{n'} \dot{F}_{n'n} = \frac{2\pi i}{h} \sum_{n'} u_{n'}(E_{n'} - E_n) F_{n'n}. \tag{27.5}$$

But by (27.2) and the energy equation $Hu_n = E_n u_n$ we have

$$\begin{aligned} HFu_n &= \sum_{n'} u_{n'} E_{n'} F_{n'n}, \\ FHu_n &= E_n F u_n = \sum_{n'} u_{n'} E_n F_{n'n} \end{aligned} \tag{27.6}$$

or

$$(HF - FH)u_n = \sum_{n'} u_{n'}(E_{n'} - E_n) F_{n'n} = \frac{h}{2\pi i} \dot{F} u_n. \tag{27.7}$$

We are thus lead, in a natural way, to the result that the time derivative $\dot{F}$ of an operator F is defined by

$$\frac{h}{2\pi i} \dot{F} = HF - FH. \tag{27.8}$$

Applying this to a coordinate and a momentum, we find

$$\frac{h}{2\pi i} \dot{q} = Hq - qH, \qquad \frac{h}{2\pi i} \dot{p} = Hp - pH. \tag{27.9}$$

This is the quantum-mechanical equivalent of Hamilton's equations $\dot{q} = \partial H/\partial p$, $\dot{p} = \partial H/\partial q$. If the operator F is explicitly dependent on t, (27.8) must be generalized to read

$$\frac{h}{2\pi i} \dot{F} = HF - FH + \frac{h}{2\pi i} \frac{\partial F}{\partial t}. \tag{27.10}$$

If we make the transition to classical mechanics in (27.8), by letting $h \to 0$, we find that $HF - FH \to 0$, which only expresses the well-known fact that all classical dynamic variables commute. In quantum mechanics, however, dynamic variables are not commutative in general, and this makes it possible to determine the equations of motion (27.8).

It follows from (27.8) that a quantity F is a constant of motion, that is, $F = 0$, if $\partial F/\partial t = 0$ and

$$HF = FH \tag{27.11}$$

if F and H commute. In this case simultaneous eigenfunctions or eigenstates u_{mn} exist for F and H: eigenfunctions satisfying the eigenvalue equations

$$\begin{aligned} Hu_{nm} &= E_n u_{nm}, \\ Fu_{nm} &= F_m u_{nm}. \end{aligned} \tag{27.12}$$

Simultaneous Eigenfunctions

Let us consider an eigenfunction u_n corresponding to the eigenvalue E_n,

$$Hu_n = E_n u_n. \tag{27.13}$$

Since F and H commute, we may write

$$H(Fu_n) = F(Hu_n) = E_n(Fu_n). \tag{27.14}$$

Hence Fu_n is an eigenfunction of the energy, just as u_n itself, with the same eigenvalue E_n.

If u_n is the only solution of the energy equation with this eigenvalue, we shall simply have

$$Fu_n = F_n u_n. \tag{27.15}$$

If this is valid for all states u_n, the operator F must (as we shall see later) be a function of the energy, and F_n a corresponding function of E_n, that is,

$$F = F(H), \qquad F_n = F(E_n). \tag{27.16}$$

Hence the application of the operator F does not furnish any new information about the states, information that is not accessible by means of the energy operator H.

Otherwise if the state u_n is composed, say, for simplicity, of two linearly independent states,

$$u_n = c_1 v_1 + c_2 v_2. \tag{27.17}$$

In this case, Fu_n must be a state with the energy $E = E_n$, by (27.14); that is, it must be a new linear combination of the states v_1 and v_2.

Hence we may write

$$\begin{aligned} Fv_1 &= v_1 F_{11} + v_2 F_{21}, \\ Fv_2 &= v_1 F_{12} + v_2 F_{22}. \end{aligned} \tag{27.18}$$

Assuming, for simplicity, that v_1 and v_2 are orthonormalized functions, we obtain

$$F_{21} = \int v_2^* F v_1 \, d\tau, \qquad F_{12} = \int v_1^* F v_2 \, d\tau, \tag{27.19}$$

or by (25.16) and the subsequent considerations,

$$F_{12} = \int v_2 F^* v_1^* \, d\tau = F_{21}^*. \tag{27.20}$$

We now apply the operator F to the state (27.17) and try to determine c_1 and c_2 in such a way that the equation

$$Fu_n = F'u_n \tag{27.21}$$

is valid for some eigenvalue F' of F. This yields

$$\begin{aligned} (F_{11} - F')c_1 + F_{12}c_2 &= 0, \\ F_{21}c_1 + (F_{22} - F')c_2 &= 0, \end{aligned} \tag{27.22}$$

that is,

$$\begin{vmatrix} F_{11} - F' & F_{12} \\ F_{21} & F_{12} - F' \end{vmatrix} = 0, \tag{27.23}$$

$$F' = \begin{pmatrix} F_1 \\ F_2 \end{pmatrix} = \frac{F_{11} + F_{22}}{2} \pm \left[\left(\frac{F_{11} - F_{22}}{2} \right)^2 + F_{12}F_{21} \right]^{1/2}.$$

Hence it follows that we may, from two linearly independent states, generate linear combinations that are eigenstates also for the operator F. This applies for any number of linearly independent states; for compound energy states u_n, we shall then obtain special linear combinations u_{nm} with given eigenvalues F_m for the operator F. These simultaneous eigenstates or eigenfunctions for the operators F and H are thus characterized by the simultaneous eigenvalue equations (27.12); the orthogonality relations

$$\int u_{n'm'}^* u_{nm} \, d\tau = 0 \qquad \text{for} \qquad E_{n'} \neq E_n \qquad \text{or} \qquad F_{m'} \neq F_m \tag{27.24}$$

then follow from these equations in the usual way.

We may show, by a procedure completely analogous to the above, that the condition that must be satisfied if two arbitrary dynamic quantities are to have simultaneous eigenfunctions or eigenstates,

$$\begin{aligned} Fu_{ml} &= F_m u_{ml}, \qquad Gu_{ml} = G_l u_{ml}, \\ \int u_{m'l'}^* u_{ml} \, d\tau &= 0, \qquad F_{m'} \neq F_m \qquad \text{or} \qquad G_{m'} \neq G_m, \end{aligned} \tag{27.25}$$

is that the two operators commute,

$$FG - GF = 0. \tag{27.26}$$

The problem of finding a complete set of constants of motion for a system thus consists of determining a set of operators $F, G, \cdots$, that are mutually

commutative and all commute with the energy operator H. This condition of commutativity restricts the number of mutually independent operators to be equal to the number of degrees of freedom for the system.

Operators and Operator Functions

Let us consider an eigenfunction u_m for the operator F,

$$Fu_m = F_m u_m. \tag{27.27}$$

Applying the operator F several times successively to (27.27), and writing $FF = F^2$, $FF^2 = F^3$, and so forth, we obtain the eigenvalue equation

$$F^n u_m = {F_m}^n u_m \tag{27.28}$$

for the operator F^n, which denotes n successive applications of the operator F. Similarly we may construct new operators by means of power series

$$f(F) = \sum_n c_n F^n, \tag{27.29}$$

which may, or may not, terminate; and also define such analytic operator functions as

$$e^F = 1 + F + \frac{1}{1 \cdot 2} F^2 + \cdots \tag{27.30}$$

The eigenvalue equations for such operators will read

$$f(F)u_m = f(F_m)u_m, \tag{27.31}$$

and hence we may define even more general operator functions than those representable by means of a power series. For such operators we require that they commute with and have the same eigenfunctions as a given operator F; the operator f is then simply defined by the eigenvalue equation (27.31) or by the functional relation between the eigenvalues

$$f_m = f(F_m). \tag{27.32}$$

Similarly we may define an operator function $f(F, G)$ of several dynamic variables F and G, namely, by the functional relation between their simultaneous eigenvalues

$$f_{ml} = f(F_m, G_l). \tag{27.33}$$

If the function f in this equation is expressible as a power series in F_m and G_m, the operator f is simply given as the corresponding power series in F and G, each power signifying the application of F and G the appropriate number of times.

Let us now assume that three operators F, G, and f all commute with each other, and with H; furthermore we assume that the simultaneous eigenfunctions u_{ml} for F and G, and the corresponding eigenvalues F_m, G_l, are

known. In this case, fu_{ml} will (as we have seen) still be an eigenfunction of both F and G, corresponding to the eigenvalues F_m and G_l. Two possibilities now exist: either fu_{ml} is identical with u_{ml}, apart from a numerical factor, or it is not. In the latter case the function u_{ml} is not uniquely defined but is composed by several linearly independent functions. These may be specified in more detail, by determining the special combinations that are also eigenfunctions for the independent operator f. In the former case, on the other hand, we have simply

$$fu_{ml} = f_{ml}u_{ml}, \tag{27.34}$$

where f_{ml} is a uniquely defined function of m and 1, and hence also of F_m and G_l. This is the situation expressed by (27.33), where f is a function of the two operators F and G,

$$f = f(F, G). \tag{27.35}$$

To illustrate these considerations let us assume that we have a free particle with the energy

$$H = \frac{1}{2m_0}(p_x^2 + p_y^2 + p_z^2). \tag{27.36}$$

This energy function commutes with each of the components of momentum but not with the coordinates x, y, z; consequently these coordinates, or functions of them, cannot be constants of the motion. On the other hand, all the three components of momentum are independent constants of the motion, since they commute both with each other and with H,

$$p_x p_y - p_y p_x = 0, \qquad \text{etc.} \tag{27.37}$$

Hence the system may be quantized with respect to the momenta by putting

$$p_x = p'_x, \qquad p_y = p'_y, \qquad p_z = p'_z, \tag{27.38}$$

where the dashed symbols denote the eigenvalues, which in this case may vary continuously in the region $-\infty \leqq p'_x, p'_y, p'_z \leqq \infty$. However, when these eigenvalues are fixed, the corresponding values of the energy operator (27.36) are also determined; that is, H is a function of the momenta, as already indicated by (27.36).

The eigenfunctions for the momenta may be written

$$\begin{aligned} \psi_x &= c_1 \exp\left(\frac{2\pi i}{h} p'_x x\right), \qquad \psi_y = c_2 \exp\left(\frac{2\pi i}{h} p'_y y\right), \\ \psi_z &= c_3 \exp\left(\frac{2\pi i}{h} p'_z z\right). \end{aligned} \tag{27.39}$$

Here the constants c_1, c_2, c_3 are to be regarded as constant only with respect

to changes in the corresponding coordinates x, y, z; we may thus, for instance, have $c_1 = f_1(y, z)$, and so on. The eigenfunctions (27.39) are consequently compatible with the hypothesis that

$$\psi = \exp\left[\frac{2\pi i}{h}(p'_x x + p'_y y + p'_z z)\right]. \tag{27.40}$$

From the equation $H\psi = E\psi$ it then follows, writing

$$p_x = \frac{h}{2\pi i}\frac{\partial}{\partial x}, \qquad \text{etc.},$$

that

$$E = \frac{1}{2m_0}(p'^2_x + p'^2_y + p'^2_z). \tag{27.41}$$

Since any dynamic variable

$$F(x, \cdots, p_x, \cdots) = F\left(x, \cdots, \frac{h}{2\pi i}\frac{\partial}{\partial x}, \cdots\right) \tag{27.42}$$

either depends only on the momenta p_x, p_y, p_z (and thus commutes with H), or contains the coordinates x, y, z (and consequently does not commute with H), it follows that all constants of the motion are functions of the three basic quantities p_x, p_y, p_z. Choosing one such function, say H, as a primary constant of the motion, we find that it is then sufficient to determine two other independent constants of the motion, say p_x and p_y; p_z is then a function of E, p_x, and p_y. The maximum number of independent constants of motion for a free particle is thus always three.

If, on the other hand, we choose to consider a single particle in a central field, it turns out that the components of angular momentum

$$m_z = xp_y - yp_x, \qquad \text{etc.},$$

and, consequently, also the square of the angular momentum

$$\mathbf{m}^2 = m_x^2 + m_y^2 + m_z^2 \tag{27.43}$$

commute with

$$H = \frac{1}{2m_0}(p_x^2 + p_y^2 + p_z^2) + V(r). \tag{27.44}$$

The individual components m_x, m_y, m_z, however, are not mutually commutative, even though they all commute with $\mathbf{m}^2$. Hence we may quantize only one of these components, say m_z; this component will then, together with $\mathbf{m}^2$ and E, constitute a set of three primary constants of the motion. The values of the quantized angular momenta have already been stated in (24.30); their deduction will be demonstrated in the following section.

CHAPTER 4

Special Atomic Problems

28. THE WAVE-MECHANICAL TREATMENT OF THE HYDROGEN ATOM

The Hamiltonian and the Wave Equation in Relative Coordinates

We consider two particles with masses m_1 and m_2, and a mutual potential energy $V = V(|\mathbf{r}_1 - \mathbf{r}_2|)$. The Hamiltonian for this system is

$$H = \frac{1}{2m_1}\mathbf{p}_1^2 + \frac{1}{2m_2}\mathbf{p}_2^2 + V, \tag{28.1}$$

and the corresponding Schrödinger equation

$$\left[\left(\frac{h}{2\pi i}\right)^2\left(\frac{1}{2m_1}\nabla_1^2 + \frac{1}{2m_2}\nabla_2^2\right) + V\right]\psi = E\psi. \tag{28.2}$$

Both the classical and quantum-mechanical treatments of problems of this kind are facilitated by the introduction of the center of mass coordinates $\mathbf{R}$ and the relative coordinates $\mathbf{r}$,

$$\mathbf{R} = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2}, \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{28.3}$$

Since $\dot{\mathbf{R}}$, $\dot{\mathbf{r}}$ and $\dot{\mathbf{r}}_1$, $\dot{\mathbf{r}}_2$ obey the same transformation equations, we must have

$$\begin{aligned} \frac{\partial}{\partial x_1} &= \frac{m_1}{m_1 + m_2}\frac{\partial}{\partial X} + \frac{\partial}{\partial x}, \qquad \frac{\partial}{\partial x_2} = \frac{m_2}{m_1 + m_2}\frac{\partial}{\partial X} - \frac{\partial}{\partial x}, \\ \frac{\partial}{\partial \dot{x}_1} &= \frac{m_1}{m_1 + m_2}\frac{\partial}{\partial X} + \frac{\partial}{\partial \dot{x}}, \qquad \frac{\partial}{\partial \dot{x}_2} = \frac{m_2}{m_1 + m_2}\frac{\partial}{\partial X} - \frac{\partial}{\partial \dot{x}}, \qquad \text{etc.} \end{aligned} \tag{28.4}$$

Hence we obtain, both for the classical definition of momentum

$$p_{x_1} = \frac{\partial T}{\partial \dot{x}_1}, \tag{28.5}$$

and the wave-mechanical definition

$$p_{x_1} = \frac{h}{2\pi i}\frac{\partial}{\partial x_1}, \tag{28.6}$$

the same equations of transformation

$$\mathbf{p}_1 = \frac{m_1}{m_1 + m_2}\mathbf{P} + \mathbf{p}, \qquad \mathbf{p}_2 = \frac{m_2}{m_1 + m_2}\mathbf{P} - \mathbf{p}. \tag{28.7}$$

Thus the Hamiltonian operator takes the form

$$H = \frac{1}{2M}\mathbf{P}^2 + \frac{1}{2\mu}\mathbf{p}^2 + V, \tag{28.8}$$

where M is the total, and μ the reduced or relative, mass of the two particles,

$$M = m_1 + m_2, \qquad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}, \tag{28.9}$$

both in the classical and wave-mechanical sense. Hence the wave equation may be written

$$\left[\left(\frac{h}{2\pi i}\right)^2\left(\frac{1}{2M}\nabla_R{}^2 + \frac{1}{2\mu}\nabla^2\right) + V\right]\psi = E\psi, \tag{28.10}$$

where ∇_R and ∇ are the gradient operators in the center of mass and relative coordinates, respectively. Exactly the same result would have been obtained by transforming (28.2) directly by means of the equations corresponding to (28.4) and (28.7), that is,

$$\nabla_1 = \frac{m_1}{m_1 + m_2}\nabla_R + \nabla, \qquad \nabla_2 = \frac{m_2}{m_1 + m_2}\nabla_R - \nabla. \tag{28.11}$$

The solution of (28.10) may be written

$$\psi = \exp\left(\frac{2\pi i}{h}\mathbf{PR}\right)\Psi(\mathbf{r}), \tag{28.12}$$

where $\mathbf{P}$ is the quantized total momentum of the system. The corresponding translational energy is

$$E_R = \frac{P^2}{2m}. \tag{28.13}$$

The three-dimensional equation for the wave function Ψ in relative coordinates is then

$$\left[\left(\frac{h}{2\pi i}\right)^2\frac{1}{2\mu}\nabla^2 + V + E_R\right]\Psi = E\Psi. \tag{28.14}$$

Since the translational motion of an atom is usually of minor importance, except in some special cases (for example, the Doppler effect), we shall put $\mathbf{P} = 0$, $E_R = 0$ for simplicity. The terms ψ and Ψ are then, by (28.12), identical; hence the wave equation for our two-particle system m_1, m_2 differs from the ordinary wave equation only by the appearance of the reduced mass μ, defined by (28.9). For an electron with mass $m_1 = m_0$ and an atomic nucleus with mass $m_2 = m_z$, this reduced mass will be given by

$$\frac{1}{\mu} = \frac{1}{m_0} + \frac{1}{m_z}. \tag{28.15}$$

Equation 28.15 leads in the usual way to a mass correction for the energy terms; this correction is identical with that which we have already met, in our deduction of the different Rydberg constants from the earlier quantum theory.

In the following we shall omit such details and replace the reduced mass μ by the rest mass m_0 of the electron. The notation m_0 is chosen to avoid confusion with the magnetic quantum number m, and (later) with the relativistic mass $m = m_0(1 - v^2/c^2)^{-1/2}$ of the electron. Considering the general Kepler problem for an electron, that is, with an atomic nucleus having the charge Ze, we then have to solve the wave equation

$$\left[\nabla^2 + \frac{8\pi^2 m_0}{h^2}\left(E + \frac{Ze^2}{r}\right)\right]\psi = 0. \tag{28.16}$$

Solution of the Wave Equation by Separation in Spherical Polar Coordinates

In order to solve (28.16) we transform it into spherical polar coordinates. We have encountered this transformation before and shall therefore assume it to be known; however, we point out that it is most easily performed by writing the operator ∇^2 as div ∇ and calculating the efflux from an element of volume

$$d\tau = r^2\, dr \sin\vartheta\, d\vartheta\, d\varphi \tag{28.17}$$

due to the gradient field $\nabla\psi$, with the components

$$\frac{\partial\psi}{\partial r}, \qquad \frac{1}{r}\frac{\partial\psi}{\partial\vartheta}, \qquad \frac{1}{r\sin\vartheta}\frac{\partial}{\partial\varphi}. \tag{28.18}$$

Since the surface elements normal to these three principal directions are

$$r^2\, d\vartheta \sin\vartheta\, d\varphi, \qquad dr\, r \sin\vartheta\, d\varphi, \qquad dr\, r\, d\vartheta,$$

we shall have

$$\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial\psi}{\partial r}$$

instead of

$$\frac{\partial^2 \psi}{\partial r^2}$$

as the contribution to $\nabla^2\psi$ due to the efflux in the r-direction, and correspondingly for the other directions. The transformed wave equation will therefore read

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2}\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta}+\frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right)+\frac{8\pi^2 m_0}{h^2}\left(E+\frac{Ze^2}{r}\right)\right]\psi=0, \quad (28.19)$$

and thus differ somewhat in form from the classical Hamiltonian in spherical polar coordinates

$$H=\frac{1}{2m_0}\left(p_r^{\,2}+\frac{1}{r^2}p_\vartheta^{\,2}+\frac{1}{r^2\sin^2\vartheta}p_\varphi^{\,2}\right)+V. \quad (28.20)$$

Equation 28.19 may be solved by separation, by putting

$$\psi=R(r)\Theta(\vartheta)\Phi(\varphi). \quad (28.21)$$

Substitution of this in (28.19) and division by ψ then leads to

$$\frac{(1/r^2)(d/dr)[r^2(dR/dr)]}{R}+\frac{1}{r^2}\left[\frac{(1/\sin\vartheta)(d/d\vartheta)\sin\vartheta\,(d\Theta/d\vartheta)}{\Theta}+\frac{1}{\sin^2\vartheta}\frac{d^2\Phi/d\varphi^2}{\Phi}\right]+\frac{8\pi^2 m_0}{h^2}\left(E+\frac{Ze^2}{r}\right)=0. \quad (28.22)$$

If we now keep the coordinates r and ϑ fixed and allow only the coordinate φ to vary, we see that (28.22) may only be satisfied if the φ-dependent part is a constant, say $-m^2$; hence we put

$$\frac{d^2\Phi}{d\varphi^2}+m^2\Phi=0. \quad (28.23)$$

Next we allow only ϑ to vary and find that the expression in brackets must be a constant, which we write as $-l(l+1)$. Hence the following equation results:

$$\left[\frac{1}{\sin\vartheta}\frac{d}{d\vartheta}\sin\vartheta\frac{d}{d\vartheta}-\frac{m^2}{\sin^2\vartheta}+l(l+1)\right]\Theta=0. \quad (28.24)$$

For the function $R(r)$ we finally obtain

$$\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{l(l+1)}{r^2}+\frac{8\pi^2 m_0}{h^2}\left(E+\frac{Ze^2}{r}\right)\right]R(r)=0. \quad (28.25)$$

The solutions of (28.23) may be uniquely represented as

$$\Phi_m = e^{im\varphi}, \tag{28.26}$$

where m may take both positive and negative values. By the general requirements previously laid down these functions must be uniquely determined, that is, periodic in φ with the period 2π. Hence the numbers m must be real integers, $m = 0, \pm 1, \pm 2, \cdots$.

Equation 28.24 is the well-known differential equation for the associated Legendre functions

$$\Theta_{lm} = P_l^m(\cos\vartheta). \tag{28.27}$$

For integral m these are regular in $\cos\vartheta = \pm 1$ only if also l is an integer. For l and m we have the relations

$$l \geqq |m|, \qquad m = -l, \cdots, 0, \cdots, l. \tag{28.28}$$

Compare Part I, (35.12). The complete definition of the functions $P_l^m(\cos\vartheta)$ and the proof that they satisfy (28.24), will be deferred until later, when we shall apply these functions to particular problems.

The most interesting equation is (28.25) which furnishes the energy of the hydrogen atom. First we introduce a new variable ρ by the equation

$$\rho = \frac{4\pi}{h}\sqrt{-2m_0E}\, r \tag{28.29}$$

for states with a negative energy; the factor of proportionality is chosen such that the constant term of the new equation becomes $-\frac{1}{4}$. By means of (28.29) and the relation

$$\frac{d}{dr} = \frac{4\pi}{h}\sqrt{-2m_0E}\,\frac{d}{d\rho} \tag{28.30}$$

we find from (28.25), after dividing by the square of the proportionality factor in (28.29) and (28.30), that

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} - \frac{1}{4} + \frac{n}{\rho}\right]R = 0, \tag{28.31}$$

$$n = \frac{2\pi}{h}\frac{m_0Ze^2}{(-2m_0E)^{1/2}}, \qquad E = -\frac{2\pi^2m_0Z^2e^4}{h^2n^2}. \tag{28.32}$$

Equation 28.31 has two singular points, $\rho = 0$ and $\rho = \infty$ at the limits of the interval; the asymptotic solutions in these two points are, respectively,

$$R = \begin{pmatrix} \rho^l \\ \rho^{-l-1} \end{pmatrix} \qquad \text{and} \qquad R = \begin{pmatrix} e^{-\rho/2} \\ e^{\rho/2} \end{pmatrix}. \tag{28.33}$$

Only two of these, ρ^l and $e^{-\rho/2}$, satisfy the requirement that the wave function be finite and uniquely determined everywhere.

Following the usual procedure for differential equations of this type, we separate out the asymptotic factors by writing

$$R = \rho^l e^{-\rho/2} y. \tag{28.34}$$

Differentiating R and substituting in (28.31), we then obtain the equation

$$\left[\frac{d^2}{d\rho^2} + \left(\frac{2l+2}{\rho} - 1\right)\frac{d}{d\rho} + \frac{n-l-1}{\rho}\right] y = 0, \tag{28.35}$$

the solution of which may be written in the form of a power series

$$y = c_0 + c_1\rho + c_2\rho^2 + \cdots. \tag{28.36}$$

In general this series will not terminate; and in this case one may show that it increases asymptotically toward a function of the order e^ρ, which once again makes the function R in (28.34) unacceptable. The only acceptable solutions are thus obtained by requiring that the series (28.36) terminate, say, with the term

$$c_{n_r}\rho^{n_r}.$$

The condition for (28.35) to be satisfied is therefore that the coefficient of ρ^{n_r-1} vanishes, that

$$-n_r + n - l - 1 = 0 \qquad \text{or} \qquad n = n_r + l + 1. \tag{28.37}$$

Since n_r represents any non-negative integral value, $n_r = 0, 1, 2, \cdots$, the number n must also be an integer,

$$n = l + 1, l + 2, \cdots, \tag{28.38}$$

or for a fixed n,

$$l = 0, 1, \cdots, n - 1. \tag{28.39}$$

By means of these quantized integral values of the parameter n, which is identical with the previous principal quantum number n, we may now use (28.32) to express the quantized energy levels in terms of the Rydberg constant. Thus

$$E_n = -\frac{Z^2 Rh}{n^2}, \qquad R = \frac{2\pi^2 m_0 e^4}{h^3}. \tag{28.40}$$

The corresponding energy states are said to be degenerate, that is, the energies of several states coincide. To each n there correspond several values of l, by (28.39) and to each l there correspond

$$2l + 1 = (l + 1)^2 - l^2 \tag{28.41}$$

values of m, as indicated in (28.28). Hence the total number of independent

states with the energy E_n is given by

$$\sum_{l=0}^{n-1} [(l+1)^2 - l^2] = n^2. \tag{28.42}$$

In the above considerations we have by separation of the wave equation in the three coordinates, r, ϑ, φ, isolated certain "partial wave equations," so to speak; in other words, we have quantized certain operators, apart from the energy by means of the quantum numbers l and m. Later we shall show that

$$\begin{aligned} m_z &= \frac{h}{2\pi i}\frac{\partial}{\partial\varphi}, \\ \mathbf{m}^2 &= \left(\frac{h}{2\pi i}\right)^2\left[\frac{\partial^2}{\partial\vartheta^2} + \frac{\cos\vartheta}{\sin\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right], \end{aligned} \tag{28.43}$$

so that the quantized values of these angular momentum operators are

$$\mathbf{m}^2 = \left(\frac{h}{2\pi}\right)^2 l(l+1), \qquad m_z = \frac{h}{2\pi} m. \tag{28.44}$$

We now write (28.29) in the form

$$\rho = \frac{2}{a} r, \tag{28.45}$$

where

$$a = \frac{h}{2\pi}\frac{1}{(-2m_0E)^{1/2}} = \left(\frac{h}{2\pi}\right)^2 \frac{n}{Zm_0e^2}$$

or

$$a_n = \frac{n}{Z} a_H, \qquad a_H = \frac{h^2}{4\pi^2 m_0 e^2}. \tag{28.46}$$

The term a_H is the well-known Bohr radius of the first circular electronic orbit of the hydrogen atom.

Concerning the functions y in (28.34) and (28.35) we shall at this stage only note that they may be deduced by means of the so-called Laguerre polynomials $L_n(x)$, defined by the differential equation

$$xL_n'' + (1-x)L_n' + nL_n = 0. \tag{28.47}$$

For the Laguerre polynomial L_{n+1} we then obtain the equation

$$xL_{n+l}'' + (1-x)L_{n+l}' + (n+l)L_{n+l} = 0, \tag{28.48}$$

and by differentiating $2l+1$ times we find that

$$\left[x\frac{d^2}{dx^2} + (2l+2-x)\frac{d}{dx} + n - l - 1\right] L_{n+l}^{2l+1}(x) = 0 \tag{28.49}$$

must hold for the $(2l + 1)$th derivative of L_{n+1}. Equation (28.49) clearly corresponds exactly to (28.35). Later we shall discuss the exact definition of these polynomials in more detail; here we only state the solutions obtained for the radial wave equation, namely,

$$R_{nl} = N_{nl}\rho^l e^{-\rho/2} L_{n+l}^{2l+1}(\rho), \tag{28.50}$$

where N_{nl} is a factor of normalization, usually chosen such that

$$\int_0^\infty R_{nl}^2 r^2 \, dr = 1.$$

The entire wave function for the Kepler problem may now be written as

$$\psi_{nlm} = N_{nlm}\rho^l e^{-\rho/2} L_{n+l}^{2l+1}(\rho) P_l^m(\cos\vartheta) e^{im\varphi},$$
$$\rho = \frac{2Z}{na_H} r, \tag{28.51}$$

where N_{nlm} is a new normalization factor, determined for the entire wave function. Since

$$d\tau = dx\, dy\, dz = r^2\, dr \sin\vartheta\, d\vartheta\, d\varphi, \tag{28.52}$$

we obtain the orthonormalization relations

$$\int \psi^*_{n'l'm'} \psi_{nlm}\, d\tau = \delta_{nn'}\, \delta_{ll'}\, \delta_{mm'}, \tag{28.53}$$

provided that

$$\int_0^\infty R_{n'l} R_{nl} r^2\, dr = \delta_{nn'}, \qquad \int_0^\pi \Theta_{'m}\Theta_{lm} \sin\vartheta\, d\vartheta = \delta_{ll'},$$
$$\int_0^{2\pi} \Phi^*_{m'}\Phi_m\, d\varphi = \delta_{mm'}, \tag{28.54}$$
$$\Theta_{lm} = \Theta_{l(-m)} = N_{lm} P_l^m(\cos\vartheta), \qquad \Phi_m = \frac{1}{(2\pi)^{1/2}} e^{im\varphi}.$$

These orthogonality properties are readily shown to be true by means of the corresponding differential equations (28.35), (28.24), and (28.23).

29. QUANTIZATION OF ANGULAR MOMENTA

Quantized angular momenta are of paramount importance in atomic theory. This is, of course, primarily connected with the fact that angular momenta have the dimension of action and are closely related to the action variables or phase integrals of quantum theory. The quantized units for angular momentum are expressed directly by the quantum of action h, being equal to $h/2\pi$.

Moreover the fundamental importance of the angular momentum is further emphasized by the fact that the so-called elementary particles have an intrinsic angular momentum or spin; thus the spin of the electron (and also of the proton and neutron) is $\frac{1}{2}$, measured in the unit mentioned above. Hence one may deduce from the spin of an atomic nucleus whether it contains an even or odd number of elementary particles; this spin will then be integral or half-integral, according to whether the nucleus has an even or odd atomic weight. Consequently atomic nuclei must be thought of as composed of protons and neutrons, and not of protons and electrons. To the spins of the individual elementary particles, of course, must be added—even within the atomic nucleus—any orbital angular momenta of these particles. However, these angular momenta are always integral and thus do not invalidate the rule stated above.

Simple Rotator with a Fixed Axis

The simplest model for a diatomic molecule is the rigid rotator which is imagined as two mass points m_1 and m_2 with a fixed mutual separation r_0. For this two-body problem the results deduced in Section 28 apply: the motion may be partitioned into the center of mass and relative motions. The former is of little interest, and we therefore consider only the kinetic energy of the relative motion which may be written

$$T = \frac{m_0}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2), \tag{29.1}$$

where m_0 is the reduced mass.

Since the motion of such a rotator will be confined to a plane in classical mechanics, one might expect that it would be sufficient to consider a rotation in, say, the xy-plane. In quantum theory, however, this does not hold; and the reason for this is that an actual measurement of an angular momentum will give rise to a change, not only in its magnitude but also in its direction. Hence the correct quantum-mechanical model is the so-called free rotator.

Nevertheless the fixed rotator (rotator with a fixed axis) does have some importance, as a model for partial problems of quantum mechanics; this, of course, also applies to several other simplified systems. We shall therefore consider it in some detail. For instance, we may substitute

$$x = r_0 \cos \varphi, \qquad y = r_0 \sin \varphi, \qquad z = 0. \tag{29.2}$$

in (29.1), thus obtaining

$$T = \frac{I}{2}\dot{\varphi}^2, \qquad I = m_0 r_0^2, \tag{29.3}$$

where I is the moment of inertia of the rotator. We now introduce the

canonically conjugate momentum to φ,

$$p_\varphi = \frac{\partial T}{\partial \dot{\varphi}} = I\dot{\varphi}, \tag{29.4}$$

which, in reality, is the angular momentum with respect to the fixed z-axis. This yields the kinetic energy, which in this case is also the total energy $H = T$, expressed in terms of p_φ,

$$H = \frac{1}{2I} p_\varphi^2. \tag{29.5}$$

The wave equation for the rotator must therefore read

$$\frac{1}{2I}\left(\frac{h}{2\pi i}\right)^2 \frac{\partial^2 \psi}{\partial \varphi^2} = E\psi. \tag{29.6}$$

with the solution

$$\psi = \psi_m = e^{im\varphi}, \tag{29.7}$$

where m may take both negative and positive integral values. The corresponding energy values are

$$E_m = \frac{h^2 m^2}{8\pi^2 I}. \tag{29.8}$$

It follows from (29.5) that H is a function of p_φ only, and thus p_φ is a function of H. We may, therefore, also quantize the angular momentum directly by

$$p_\varphi \psi = p'_\varphi \psi \qquad \text{or} \qquad \frac{h}{2\pi i}\frac{\partial \psi}{\partial \varphi} = p'_\varphi \psi. \tag{29.9}$$

This equation has the same solutions as the energy equation, namely, ψ_m in (29.7); hence the quantized angular momenta are

$$p'_\varphi = m\frac{h}{2\pi}, \qquad m = \cdots, -1, 0, 1, \cdots. \tag{29.10}$$

The Free Rotator

For the free rotator we may reexpress the equation (29.1) for the kinetic energy by transforming to spherical polar coordinates r, ϑ, φ right away, and then reduce the number of variables to two by putting $r = r_0 = \text{const}$. We must, however, be careful not to introduce any ambiguity into the wave equation by means of Hamiltonians which contain both momenta and coordinates in the kinetic energy. We therefore employ the Cartesian momenta and write

$$H = T = \frac{1}{2m_0}(p_x^2 + p_y^2 + p_z^2). \tag{29.11}$$

From the defining equation of angular momentum

$$\mathbf{m} = \mathbf{r} \times \mathbf{p} \tag{29.12}$$

we may deduce, classically, the relation

$$\mathbf{m}^2 = r^2p^2 - (\mathbf{rp})^2. \tag{29.13}$$

For a constant $r = r_0$ and $\mathbf{r} \cdot \mathbf{p} = rp_r = 0$ this leads to

$$\mathbf{m}^2 = r_0^2p^2 \tag{29.14}$$

or

$$H = \frac{1}{2I}\mathbf{m}^2, \qquad I = m_0r_0^2, \tag{29.15}$$

where I is the moment of inertia of the rotator. Because of the commutation properties of coordinates and momenta, (29.13) is not a correct quantum-mechanical equation; however, (29.14) is valid [and hence also (29.15)], an assertion of which we shall not give any proof here. Comparison with the wave-mechanical operator in (28.19), where we put $\partial/\partial r = 0$ and $r = r_0$, then shows that the differential operator for $\mathbf{m}^2$ is given by

$$\mathbf{m}^2 = \left(\frac{h}{2\pi i}\right)^2\left(\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right). \tag{29.16}$$

From

$$x = r_0\sin\vartheta\cos\varphi, \qquad y = r_0\sin\vartheta\sin\varphi, \qquad z = r_0\cos\vartheta \tag{29.17}$$

it follows, furthermore, that

$$\frac{\partial}{\partial\varphi} = x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \qquad \text{or} \qquad m_z = \frac{h}{2\pi i}\frac{\partial}{\partial\varphi}. \tag{29.18}$$

It is evident from this that $\mathbf{m}^2$ and m_z commute; hence $\mathbf{m}^2$ commutes with each of its components.

We shall now show that m_z and $\mathbf{m}^2$ have the quantized values

$$m_z = m\frac{h}{2\pi}, \qquad \mathbf{m}^2 = l(l+1)\left(\frac{h}{2\pi}\right)^2, \tag{29.19}$$

where m and l are integers such that

$$l = 0, 1, \cdots, \qquad m = -l, -l+1, \cdots, 0, \cdots, l-1, l. \tag{29.20}$$

For the eigenfunctions of m_z we obtain the equation, and solution,

$$\frac{1}{i}\frac{\partial\psi_m}{\partial\varphi} = m\psi_m, \qquad \psi_m = e^{im\varphi}; \tag{29.21}$$

the requirement that this function be uniquely defined (for rotation about the z-axis) then leads to the result that ψ_m must be periodic in φ, and hence m an integer.

The eigenvalue equation for $\mathbf{m}^2$ must by (29.16) and (29.19) read

$$\left[\frac{\partial^2}{\partial\vartheta^2} + \frac{\cos\vartheta}{\sin\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} + l(l+1)\right]\psi = 0. \tag{29.22}$$

This equation is separable in ϑ and φ, and the φ-dependence may be expressed by the eigenfunctions (29.21); hence we may write the eigenfunctions for given values of l and m as

$$\psi_{lm} = P_l^m(\cos\vartheta)e^{im\varphi}. \tag{29.23}$$

The ϑ-dependent function is to be determined by (29.22); this is, however, the well-known equation for the Legendre spherical functions. It has no regular solutions for $\vartheta = 0$ or $\vartheta = \pi$, that is, for $\cos\vartheta = \pm 1$, except when l is a non-negative integer. Putting $\xi = \cos\vartheta$, (29.22) may be written

$$\left[(1-\xi^2)\frac{d^2}{d\xi^2} - 2\xi\frac{d}{d\xi} - \frac{m^2}{1-\xi^2} + l(l+1)\right]P_l^m(\xi) = 0. \tag{29.24}$$

A detailed treatment of this equation is given in Part I, and will not be repeated here. One easily finds that the asymptotic solutions in the singular points $\xi = \pm 1$ must be $(1-\xi)^{\pm(m/2)}$ and $(1+\xi)^{\pm(m/2)}$, so that the regular solution must contain the factor $(1-\xi^2)^{m/2}$. We shall here content ourselves with stating the solution in a form that allows us straight away to deduce all its relevant properties, such as integrals of normalization, and so on,

$$\begin{aligned} P_l^m(\xi) &= (1-\xi^2)^{m/2}P_l^{(m)}(\xi), \qquad P_l^{(m)}(\xi) = \frac{d^m}{d\xi^m}P_l(\xi), \\ P_l(\xi) &= \frac{1}{2^l l!}\frac{d^l}{d\xi^l}(\xi^2-1)^l. \end{aligned} \tag{29.25}$$

It follows from (29.15) and (29.19) that the energy values for the free rotator, which do not depend on the quantum number m for the z-component of the angular momentum, is given by

$$E_{lm} = \frac{h^2}{8\pi^2 I}l(l+1). \tag{29.26}$$

The validity of this formula—in contrast to the expression (29.8) for the fixed rotator—when applied to molecules, has been very satisfactorily verified by experimental observation of the molecular band spectra.

30. GENERAL QUANTIZATION OF SIMPLE AND COMPOUND ANGULAR MOMENTA

The problem of quantizing angular momenta is one of the most fundamental in quantum mechanics. All elementary particles are, apart from their various other properties, characterized by their intrinsic spins. Compound particles, such as simple atomic nuclei or an atom with its orbital electrons in a given state, all have a definite spin. It is a notable feature of the total spin of several particles that it obeys the same laws as the spins of the individual particles; hence the addition of spins poses a very important problem. Moreover even the spin of single particles has some surprising properties. From the general laws governing the behavior of spins one may deduce both integral and half-integral spin quanta. Experience shows that nature has made use of both of these possibilities; the most characteristic elementary example is the intrinsic spin of the electron which is half-integral.

In the following we shall simplify the notation by using so-called atomic units for spins and angular momenta, that is, by taking the quantity $h/2\pi$ to equal unity; in the new units the angular momentum vectors will be denoted by $\mathbf{M}$, thus

$$\mathbf{m} = \frac{h}{2\pi}\mathbf{M}. \tag{30.1}$$

We shall also use the designation spin or angular momentum for the vector $\mathbf{M}$; in ordinary units we then have

$$\mathbf{M} = \frac{1}{i}(\mathbf{r} \times \nabla). \tag{30.2}$$

To start with, we express the spin in spherical polar coordinates, as illustrated in Fig. 4-1.

Utilizing the unit vectors $\mathbf{i}_r$, $\mathbf{i}_\vartheta$, $\mathbf{i}_\varphi$ in the three coordinate directions, we

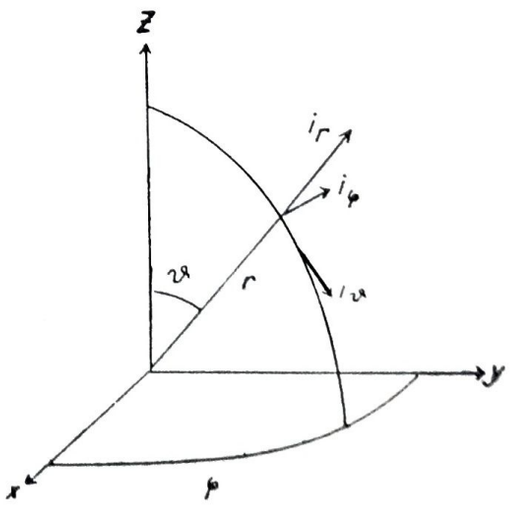

Fig. 4-1. Unit vectors in spherical polar coordinates.

may write $\mathbf{r}$ and ∇ as

$$\mathbf{r} = r\mathbf{i}_r, \qquad \nabla = \mathbf{i}_r \frac{\partial}{\partial r} + \mathbf{i}_\vartheta \frac{1}{r}\frac{\partial}{\partial \vartheta} + \mathbf{i}_\varphi \frac{1}{r \sin \vartheta}\frac{\partial}{\partial \varphi}. \tag{30.3}$$

Hence, using (30.2),

$$\mathbf{M} = \frac{1}{i}\left(\mathbf{i}_\varphi \frac{\partial}{\partial \vartheta} - \mathbf{i}_\vartheta \frac{1}{\sin \vartheta}\frac{\partial}{\partial \varphi}\right) \tag{30.4}$$

in accordance with the fact that the spin must be perpendicular to $\mathbf{r}$, by (30.2). For the Cartesian components we find by geometrical considerations that

$$\begin{aligned} M_x &= \frac{1}{i}\left(-\sin \varphi \frac{\partial}{\partial \vartheta} - \cos \varphi \frac{\cos \vartheta}{\sin \vartheta}\frac{\partial}{\partial \varphi}\right), \\ M_y &= \frac{1}{i}\left(\cos \varphi \frac{\partial}{\partial \vartheta} - \sin \varphi \frac{\cos \vartheta}{\sin \vartheta}\frac{\partial}{\partial \varphi}\right), \\ M_z &= \frac{1}{i}\frac{\partial}{\partial \varphi}. \end{aligned} \tag{30.5}$$

We now take advantage of the relation

$$[M_z, f] = M_z f - f M_z = \frac{1}{i}\frac{\partial f}{\partial \varphi}, \tag{30.6}$$

where $[M_z, f]$ is called the commutator of M_z and f. From (30.5) one easily deduces that

$$[M_z, M_x] = iM_y, \qquad [M_z, M_y] = -iM_z. \tag{30.7}$$

These equations, of which we only need one, are evidently quite general and independent of the spherical polar coordinates chosen; hence we may obtain the third equation by a cyclic permutation.

From

$$x = r \sin \vartheta \cos \varphi, \qquad y = r \sin \vartheta \sin \varphi, \qquad z = r \cos \vartheta, \tag{30.8}$$

it now follows similarly that

$$[M_z, x] = iy, \qquad [M_z, y] = -ix, \qquad [M_z, z] = 0, \tag{30.9}$$

and using the Cartesian components of ∇,

$$\begin{aligned} \frac{\partial}{\partial x} &= \cos \varphi \sin \vartheta \frac{\partial}{\partial r} + \cos \varphi \cos \vartheta \frac{1}{r}\frac{\partial}{\partial \vartheta} - \frac{\sin \varphi}{r \sin \vartheta}\frac{\partial}{\partial \varphi}, \\ \frac{\partial}{\partial y} &= \sin \varphi \sin \vartheta \frac{\partial}{\partial r} + \sin \varphi \cos \vartheta \frac{1}{r}\frac{\partial}{\partial \vartheta} + \frac{\cos \varphi}{r \sin \vartheta}\frac{\partial}{\partial \varphi}, \\ \frac{\partial}{\partial z} &= \cos \vartheta \frac{\partial}{\partial r} - \sin \vartheta \frac{1}{r}\frac{\partial}{\partial \vartheta}, \end{aligned} \tag{30.10}$$

$$\left[M_z, \frac{\partial}{\partial x}\right] = i\frac{\partial}{\partial y}, \qquad \left[M_z, \frac{\partial}{\partial y}\right] = -i\frac{\partial}{\partial x}, \qquad \left[M_z, \frac{\partial}{\partial z}\right] = 0. \tag{30.11}$$

All of these commutators are formally almost identical; the only thing to note is the sign (+) or (−) for a "positive" (x, y, z) or "negative" (z, y, x) order of coordinates or indices, obtainable by cyclic permutations. This also applies to equations of the form

$$[y, M_z] = ix, \qquad \left[\frac{\partial}{\partial x}, M_z\right] = -i\frac{\partial}{\partial y}, \qquad \text{etc.} \tag{30.12}$$

The formula for the operator $\mathbf{M}^2$ is most easily found by calculating the Eulerian variational derivative of a function ψ by means of the "element of volume" $\sin\vartheta\, d\vartheta\, d\varphi$ on a spherical surface, utilizing the expression

$$-(\mathbf{M}\psi)^2 = \left(\frac{\partial\psi}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\left(\frac{\partial\psi}{\partial\varphi}\right)^2 \tag{30.13}$$

which is obtainable from (30.5). We shall, however, proceed somewhat more directly, employing a method that will prove to be very useful later on. By means of the commutation relation

$$M_xM_y - M_yM_x = iM_z \tag{30.14}$$

we find that $\mathbf{M}^2$ may be written in two ways:

$$\begin{aligned}\mathbf{M}^2 &= (M_x - iM_y)(M_x + iM_y) + M_z + M_z^2\\ &= (M_x + iM_y)(M_x - iM_y) - M_z + M_z^2.\end{aligned} \tag{30.15}$$

The complex operators in (30.15) are by (30.5),

$$\begin{aligned}M_x + iM_y &= e^{i\varphi}\left(\frac{\partial}{\partial\vartheta} - \frac{\cos\vartheta}{\sin\vartheta}\frac{1}{i}\frac{\partial}{\partial\varphi}\right),\\ M_x - iM_y &= e^{-i\varphi}\left(-\frac{\partial}{\partial\vartheta} - \frac{\cos\vartheta}{\sin\vartheta}\frac{1}{i}\frac{\partial}{\partial\varphi}\right),\end{aligned} \tag{30.16}$$

from which one easily finds by elementary methods of calculus that, say, the first expression (30.15) leads to the operator equation

$$\mathbf{M}^2 = -\left(\frac{\partial^2}{\partial\vartheta^2} + \frac{\cos\vartheta}{\sin\vartheta}\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}\right). \tag{30.17}$$

In order to determine the eigenvalues of this operator we proceed in the following "matrix-mechanical" way. Using (30.16) and (30.6), we find that

$$\begin{aligned}M_z(M_x + iM_y) - (M_x + iM_y)M_z &= (M_x + iM_y),\\ M_z(M_x - iM_y) - (M_x - iM_y)M_z &= -(M_x - iM_y).\end{aligned} \tag{30.18}$$

We now take the states for quantized angular momenta to be characterized by symbols Φ^m, where m denotes the quantized value of M_z,

$$M_z\Phi^m = m\Phi^m. \tag{30.19}$$

We do not know, as yet, whether m is integral or not.

However, applying the first equation (30.18), we obtain

$$(M_z - m - 1)(M_x + iM_y)\Phi^m = 0. \tag{30.20}$$

Hence $(M_x + iM_y)\Phi^m$ must also be an eigenfunction for the operator M_z, which for this state takes the value

$$M_z = m' = m + 1. \tag{30.21}$$

In other words the eigenvalues for M_z are separated by intervals $\Delta m = 1$. We may therefore put

$$(M_x + iM_y)\Phi^m = (M_x + iM_y)_{m+1m}\Phi^{m+1}, \tag{30.22}$$

where the factor on the right-hand side is a numerical constant which we write in the form of a matrix element. Thus the operator $M_x + iM_y$ has the effect of "raising" an eigenfunction or -state one step.

Similarly we find

$$(M_x - iM_y)\Phi^m = (M_x - iM_y)_{m-1m}\Phi^{m-1}. \tag{30.23}$$

We now assume that the system of states considered is bounded and that there exist a highest state Φ^l and a lowest state $\Phi^{-l'}$. This means that

$$(M_x + iM_y)\Phi^l = 0, \qquad (M_x - iM_y)\Phi^{-l'} = 0 \tag{30.24}$$

whence by (30.15) and (30.19),

$$\mathbf{M}^2\Phi^l = l(l+1)\Phi^l, \qquad \mathbf{M}^2\Phi^{-l'} = l'(l'+1)\Phi^{-l'}. \tag{30.25}$$

These are the quantized values of the spin squared which must be the same for both functions; hence

$$l' = l \qquad \text{and} \qquad l - (-l') = 2l = \text{an integer}.$$

It follows that l must be integral,

$$l = 0, 1, 2, \cdots,$$

or half-integral,

$$l = \tfrac{1}{2}, \tfrac{3}{2}, \cdots.$$

For the orbital angular momenta of a single particle, only the first case occurs, since (as we have seen) the eigenfunctions $\Phi^m = e^{im\varphi}$ are unique only for the integral m. However, since the intrinsic spin has a somewhat more complicated origin than the purely orbital spin, we must in general allow for the possibility of both integral and half-integral spin quantum numbers.

By general considerations of matrix elements we may assume that $(M_x + iM_y)_{m+1m}$ and $(M_x - iM_y)_{mm+1}$ are complex conjugate quantities. Utilizing the first expression (30.15) for the operator $\mathbf{M}^2$, we then find for a

fixed $\mathbf{M}^2 = l(l+1)$ that

$$|(M_x - iM_y)_{mm+1}| = |(M_x + iM_y)_{m+1m}| = [l(l+1) - m(m+1)]^{1/2}, \tag{30.26}$$

irrespective of whether the spin quantum numbers are integral or half-integral. These matrix elements lie in one of the neighboring rows to the diagonal. The M_z-matrix is diagonal with the elements $(M_z)_{mm} = m$.

The Electron Spin Expressed by Matrices

The preceding considerations clearly indicate that the matrix elements have an intrinsic physical significance, irrespective of whether one is able to express the eigenstates in the form of ordinary eigenfunctions of known variables. This yields the possibility of describing the electronic spin by means of a formalism that has turned out to be extremely useful.

By the hypothesis of electronic spins, based on the experimental study of atomic line spectra, the anomalous Zeeman effect, and so forth, the electron has an intrinsic spin or an intrinsic rotation with the maximum spin value $\frac{1}{2}$. Hence in this case it is possible to describe the spin of the electron by an operator

$$\boldsymbol{\sigma} = 2\mathbf{M} \tag{30.27}$$

which is twice the angular momentum. Then σ_z has the value ± 1, while

$$\begin{aligned} (M_x + iM_y)_{\frac{1}{2},-\frac{1}{2}} &= 1, \qquad (M_x - iM_y)_{\frac{1}{2},-\frac{1}{2}} = 0, \\ (\sigma_x + i\sigma_y)_{1,-1} &= 2, \qquad (\sigma_x - i\sigma_y)_{1,-1} = 0. \end{aligned} \tag{30.28}$$

by (30.26). This yields the matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{30.29}$$

when we in accordance with customary usage write the lowest eigenvalue of σ_z last.

These matrices are often denoted by

$$\sigma_1, \sigma_2, \sigma_3.$$

Apart from the properties

$$\begin{aligned} \sigma_1\sigma_2 - \sigma_2\sigma_1 &= 2i\sigma_3, \qquad \text{etc.} \\ \sigma_1^2 + \sigma_2^2 + \sigma_3^2 &= 3, \end{aligned} \tag{30.30}$$

that follow from our general considerations, the σ-matrices have the following special properties,

$$\sigma_1\sigma_2 = i\sigma_3 = -\sigma_2\sigma_1, \qquad \text{etc.}, \tag{30.31}$$

and

$$\sigma_1^2 = \sigma_2^2 = \sigma_3^2 = 1 \tag{30.32}$$

which are easily verified. Hence they constitute a set of two-dimensional anticommutative operators with the square unity. In Dirac's relativistic wave equation for the electron we shall encounter some more general anticommutative operators, which may be represented by four-dimensional matrices.

Addition of Angular Momenta

We consider the compound angular momentum vector

$$\mathbf{M} = \mathbf{M}_1 + \mathbf{M}_2, \tag{30.33}$$

where $\mathbf{M}_1$ and $\mathbf{M}_2$ are angular momenta of different origins, for example, the orbital spins of two different particles, or the orbital and intrinsic spin of one particle. The components of the two vectors commute so that

$$[M_x, M_y] = [M_{1x}, M_{1y}] + [M_{2x}, M_{2y}] = i(M_{1z} + iM_{2z}) = iM_z. \tag{30.34}$$

Hence compound spins obey exactly the same laws as individual spins and have the same integral or half-integral quantized values. This is important, since it is, as a rule, only the total spin that commutes with the energy function. Thus the total spin is a constant of the motion, which may be quantized, while the individual spins are (usually) not constants of the motion.

Let us now assume that two spins of magnitudes $\mathbf{M}_1^2 = l_1(l_1 + 1)$ and $\mathbf{M}_2^2 = l_2(l_2 + 1)$ are to be added. Separately considered, each of these may be described by $2l_1 + 1$ states $\Phi_{l_1}{}^{m_1}(1)$ and $2l_2 + 1$ states $\Phi_{l_2}{}^{m_2}(2)$. Altogether, then, we obtain $(2l_1 + 1)(2l_2 + 1)$ compound states $\Phi_{l_1}{}^{m_1}\Phi_{l_2}{}^{m_2}$ with several different values of the total spin. If, say, $l_1 > l_2$, it is natural to assume that the total spin value may range from $l = l_1 - l_2$ to $l = l_1 + l_2$ over all intermediate values which are separated by unity. Each of these total spin values has a multiplicity of $2l + 1$ corresponding to the quantized values of M_z. This assumption yields the correct number of states

$$\sum_{l=l_1-l_2}^{l_1+l_2} [(l + 1)^2 - l^2] = (l_1 + l_2 + 1)^2 - (l_1 - l_2)^2 = (2l_1 + 1)(2l_2 + 1). \tag{30.35}$$

Hence the total spin is integral or half-integral, according as l_1 and l_2 are both integral or half-integral, or only one of them is half-integral.

We shall indicate briefly how one may justify the assumption just made. Let us first consider the state $\Phi_{l_1}{}^{l_1}\Phi_{l_2}{}^{l_2}$ with the maximum spin component in the z-direction. By (30.26) we then have

$$(M_{1x} + iM_{1y})\Phi_{l_1}{}^{l_1} = 0, \qquad (M_{2x} + iM_{2y})\Phi_{l_2}{}^{l_2} = 0, \tag{30.36}$$

and hence

$$(M_x + iM_y)\Phi_{l_1}^{l_1}\Phi_{l_2}^{l_2} = 0. \tag{30.37}$$

On the other hand, the quantized value of the z-component is

$$M_z = l_1 + l_2 \tag{30.38}$$

which by the general equation (30.15) leads to

$$\mathbf{M}^2 = M_z + M_z^2 = (l_1 + l_2)(l_1 + l_2 + 1). \tag{30.39}$$

For the states $\Phi_{l_1}^{l_1-1}\Phi_{l_2}^{l_2}$ and $\Phi_{l_1}^{l_1}\Phi_{l_2}^{l_2-1}$ we have $M_z = l_1 + l_2 - 1$. By a linear combination of these two states one may obtain two quantized states for the spin magnitude squared, which in both cases must be at least $(l_1 + l_2 - 1)(l_1 + l_2)$. It is very easy to show that the two quantized values must be $(l_1 + l_2 - 1)(l_1 + l_2)$ and $(l_1 + l_2)(l_1 + l_2 + 1)$.

In this way we may order the entire system. At each step we obtain the state $\mathbf{M}^2 = (l_1 + l_2)(l_1 + l_2 + 1)$ with M_z-values decreasing successively from $M_z = l_1 + l_2$ to $M_z = -(l_1 + l_2)$. Simultaneously new states appear with lower spins. The total spin for orbital angular momenta,

$$\mathbf{M}^2 = l(l + 1), \qquad l = |l_1 - l_2|, \cdots, l_1 + l_2 - 1, l_1 + l_2, \tag{30.40}$$

characterizes the state as an S-, P-, D-, or F-state, according as $l = 0, 1, 2, 3, \cdots$. If the two particles are the outer electrons of an atom, one of them will very often be in an S-state, that is, $l_1 = 0$; the state (with respect to orbital angular momentum) will then be characterized by the orbital spin, that is, the azimuthal quantum number $l_2 = 0, 1, 2, \cdots$ of the other electron alone.

Addition of the Intrinsic Spins of Two Electrons

The two spin states of a single electron may be described by two symbols, say α and β, which may be thought of as orthogonal unit vectors in a two-dimensional "spin space."

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{30.41}$$

As spin operators we may take our spin matrices σ; alternatively we might use the actual spin operators $\mathbf{s} = (h/4\pi)\boldsymbol{\sigma}$ or $\mathbf{S} = \frac{1}{2}\boldsymbol{\sigma}$. For the latter the relations (30.26) may be employed. If $\mathbf{S}$ is the spin operator for a single electron, it follows from (30.22) and (30.23) that

$$\begin{aligned} &(S_x + iS_y)\alpha = 0, \qquad (S_x - iS_y)\alpha = \beta, \qquad S_z\alpha = \tfrac{1}{2}\alpha, \\ &(S_x + iS_y)\beta = \alpha, \qquad (S_x - iS_y)\beta = 0, \qquad S_z\beta = -\tfrac{1}{2}\beta. \end{aligned} \tag{30.42}$$

We now consider the four compound spin functions for two electrons

$$\Phi_0^{\,0} = \frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}}$$

$$\Phi_1^{\,1} = \alpha(1)\alpha(2), \qquad \Phi_1^{\,0} = \frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}}, \qquad \Phi_1^{\,-1} = \beta(1)\beta(2). \tag{30.43}$$

To these functions we apply the compound spin operator

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2. \tag{30.44}$$

It is then easily seen by means of (30.42) that all the three components $S_x + iS_y$, $S_x - iS_y$, S_z, have zero values for the antisymmetrical state $\Phi_0^{\,0}$. This state may be said to have been produced by antiparallel addition of the spins of the two individual electrons, and the resulting total spin is zero.

For the symmetrical states corresponding to the parallel addition of the two electron spins, we obtain by (30.42) and (30.44)

$$\begin{gathered}
(S_x + iS_y)\Phi_1^{\,1} = 0, \qquad (S_x + iS_y)\Phi_1^{\,0} = \sqrt{2}\,\Phi_1^{\,1}, \\
(S_x + iS_y)\Phi_1^{\,-1} = \sqrt{2}\,\Phi_1^{\,0}, \qquad (S_x - iS_y)\Phi_1^{\,1} = \sqrt{2}\,\Phi_1^{\,0}, \\
(S_x - iS_y)\Phi_1^{\,0} = \sqrt{2}\,\Phi_1^{\,-1}, \qquad (S_x - iS_y)\Phi_1^{\,-1} = 0, \\
S_z\Phi_1^{\,1} = \Phi_1^{\,1}, \qquad S_z\Phi_1^{\,0} = 0, \qquad S_z\Phi_1^{\,-1} = -\Phi_1^{\,-1}.
\end{gathered} \tag{30.45}$$

Writing the spin magnitude squared in the form previously employed for $\mathbf{M}^2$,

$$\begin{aligned}
\mathbf{S}^2 &= (S_x - iS_y)(S_x + iS_y) + S_z + S_z^2 \\
&= (S_x + iS_y)(S_x - iS_y) - S_z + S_z^2,
\end{aligned} \tag{30.46}$$

it is easily seen that it takes the value $\mathbf{S}^2 = 2$ in all these three cases. The matrix representation of $\mathbf{S}$ is then by (30.45),

$$(S_x + iS_y) = \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix}, \qquad (S_x - iS_y) = \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix},$$

$$S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{30.47}$$

in agreement with the general theory [compare (30.26)] for spin matrices.

Writing the squared spin in the general form

$$\mathbf{S}^2 = S(S + 1), \tag{30.48}$$

we find the possible values

$$S = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \cdots \tag{30.49}$$

for the total spin quantum number. Addition of this spin to the orbital angular momentum may be performed in 1, 2, 3, 4, 5, $\cdots$ different ways, in the order stated above. The order of magnitude of the energy difference between these various states is such that it shows up in the fine structure of the spectral lines or terms. Hence the spin quantum number determines the so-called multiplet structure. Corresponding to the spin values (30.49) we obtain singlet, doublet, triplet, and so forth, states. The hydrogen atom with $S = \frac{1}{2}$ yields doublets, the alkali atoms likewise. The helium atom, with two orbital electrons, yields singlet terms ($S = 0$) and triplet terms ($S = 1$).

31. CALCULATION OF MATRIX ELEMENTS

Matrix-Mechanical Quantization of the Harmonic Oscillator

We have previously given a detailed description of the harmonic oscillator, determining both its energy levels and the matrix elements for quantum transitions between these levels. Now once again we discuss the harmonic oscillator, since it affords a clear and useful example of the more direct matrix-mechanical method of quantizing atomic systems.

Concerning the classical description of the harmonic oscillator we already know that the motion is harmonic with a fixed frequency ν_0. The amplitudes for p_x and x are found by means of the Hamiltonian

$$H = \frac{1}{2m} p_x^2 + \frac{m}{2} (2\pi\nu_0)^2 x^2 = E. \tag{31.1}$$

We may take p_x and x to be given by, respectively, the cosine and sine of $2\pi\nu_0 t$, and express them as follows

$$p_x = \left(\frac{mE}{2}\right)^{1/2} (e^{2\pi i\nu_0 t} + e^{-2\pi i\nu_0 t}), \qquad x = \frac{1}{2\pi i\nu_0 m} \left(\frac{mE}{2}\right)^{1/2} (e^{2\pi i\nu_0 t} - e^{-2\pi i\nu_0 t}). \tag{31.2}$$

By the correspondence principle the two exponential functions in these expressions will be connected with quantum transitions (in both directions) between neighboring states n and $n + 1$, and the amplitudes will be connected with the corresponding matrix elements. Further, assuming that the correct matrix elements are obtained by using the mean value of the energy for the two quantized states

$$\tfrac{1}{2}(E_n + E_{n+1}) = (n + 1)h\nu_0, \tag{31.3}$$

we find that

$$(p_x)_{n+1n} = (p_x)_{nn+1} = \left[\frac{(n+1)mh\nu_0}{2}\right]^{1/2},$$
$$x_{n+1n} = -x_{nn+1} = \frac{1}{2\pi i}\left[\frac{(n+1)h}{2m\nu_0}\right]^{1/2}, \tag{31.4}$$

or

$$|x_{n+1n}| = \left[\frac{(n+1)h}{8\pi^2 m\nu_0}\right]^{1/2}.$$

We shall now see that it is possible to deduce both the matrix elements (31.4) and the energy levels of the oscillator, using only the general quantization condition, the commutator

$$p_x x - x p_x = \frac{h}{2\pi i}, \tag{31.5}$$

but not employing analytical (wave-mechanical) methods. The argument becomes very simple if we write the Hamiltonian (31.1) in two different ways

$$H + \frac{1}{2}h\nu_0 = \frac{1}{2m}(p_x - i\omega_0 mx)(p_x + i\omega_0 mx),$$
$$H - \frac{1}{2}h\nu_0 = \frac{1}{2m}(p_x + i\omega_0 mx)(p_x - i\omega_0 mx), \tag{31.6}$$

where $\omega_0 = 2\pi\nu_0$. Multiplying these expressions by the compound operators for p_x and x, from the right and from the left, we then easily obtain the important commutation relations

$$(H - \tfrac{1}{2}h\nu_0)(p_x + i\omega_0 mx) - (p_x + i\omega_0 mx)(H + \tfrac{1}{2}h\nu_0) = 0,$$
$$(H + \tfrac{1}{2}h\nu_0)(p_x - i\omega_0 mx) - (p_x - i\omega_0 mx)(H - \tfrac{1}{2}h\nu_0) = 0. \tag{31.7}$$

We now recall the previous definition [(26.10) and (26.11)] of the matrix elements

$$(p_x + i\omega_0 mx)\psi_n = \sum \psi_{n'}(p_x + i\omega_0 mx)_{n'n}, \tag{31.8}$$

where ψ_n represents the quantized energy states and may be regarded as identical with the normalized wave-mechanical eigenfunctions. Thus we have, in general,

$$H\psi_n = E_n\psi_n, \qquad H\psi_{n'} = E_{n'}\psi_{n'}. \tag{31.9}$$

Applying the zero operators (31.7) to the states ψ_n and ψ_{n+1}, respectively, we obtain the conditional equations

$$(E_{n'} - E_n - h\nu_0)(p_x + i\omega_0 mx)_{n'n} = 0,$$
$$(E_{n'} - E_{n+1} + h\nu_0)(p_x - i\omega_0 mx)_{n'n+1} = 0. \tag{31.10}$$

by means of (31.8) and (31.9). It follows from these equations that all matrix elements are zero, except those for which $E_{n'} = E_n + h\nu_0$ or $E_{n'} = E_{n+1} - h\nu_0$. Hence we may conclude that the energy levels are separated by intervals $h\nu_0$, and that the matrix elements exist only for pairs of neighboring states. In the first equation (31.10) we must therefore put $n' = n + 1$ and in the second $n' = n$. Thus the energy of the states may be written

$$E_n = E_0 + nh\nu_0, \tag{31.11}$$

where E_0 is the energy of the lowest (ground) state; such a state must exist, since the energy must be positive, due to the form of the energy function.

We denote this state by ψ_0 and note that by the last equation (31.10),

$$(p_x - i\omega_0 mx)\psi_0 = 0, \tag{31.12}$$

since the state ψ_{-1} does not exist. Applying the last operator (31.6) to ψ, it then follows that

$$E_0 = \tfrac{1}{2}h\nu_0, \qquad E_n = (n + \tfrac{1}{2})h\nu_0. \tag{31.13}$$

We now apply the first operator (31.6) to an arbitrary state ψ_n, obtaining

$$2m(n + 1)h\nu_0 = (p_x - i\omega_0 mx)_{nn+1}(p_x + i\omega_0 mx)_{n+1n}. \tag{31.14}$$

Since the left-hand side is real, this implies that the two matrix elements are complex conjugate to one another; this also follows from our previous general consideration of matrix elements. We may then take them to be real and equal, that is, choose the (arbitrary) phase factor as $e^{i\eta} = 1$, $\eta = 0$.

This leads to

$$\begin{aligned}(p_x - i\omega_0 mx)_{nn+1} &= (p_x + i\omega_0 mx)_{n+1n} = [2(n + 1)mh\nu_0]^{1/2},\\ (p_x + i\omega_0 mx)_{nn+1} &= (p_x - i\omega_0 mx)_{n+1n} = 0.\end{aligned} \tag{31.15}$$

Hence by calculating the matrix elements for the operators p_x and x we obtain the results already stated in (31.4).

Calculation of Matrix Elements for the Free Rotator

The wave-mechanical eigenfunctions for the free rotator, or generally for a single particle with a given angular momentum, may be written in the normalized form

$$\Phi_l^m = (2\pi)^{-1/2} N_{lm} P_l^m(\cos\vartheta) e^{im\varphi}, \tag{31.16}$$

where the N_{lm} are factors of normalization. The calculation of the matrix elements for the three coordinate combinations

$$\begin{aligned}X + iY &= \frac{x + iy}{r} = \sin\vartheta e^{i\varphi}, \qquad X - iY = \frac{x - iy}{r} = \sin\vartheta e^{-i\varphi},\\ Z &= \frac{z}{r} = \cos\vartheta,\end{aligned} \tag{31.17}$$

is easily performed if we assume that certain fundamental formulas for the Legendre functions $P_l^m(\cos\vartheta)$ are known. One of these is the normalization integral

$$\int_0^\pi [P_l^m(\cos\vartheta)]^2 \sin\vartheta\, d\vartheta = \frac{2}{2l+1}\frac{(l+m)!}{(l-m)!} \tag{31.18}$$

which yields the factors of normalization

$$N_{lm} = \left[\frac{2l+1}{2}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}. \tag{31.19}$$

The other are the formulas of recursion and differentiation

$$\begin{aligned}
(2l+1)\xi P_l^{(m)} &= (l+1-m)P_{l+1}^{(m)} + (l+m)P_{l-1}^{(m)},\\
(2l+1)P_{l+1}^{(m)} &= P_{l+1}^{(m+1)} - P_{l-1}^{(m+1)},\\
(2l+1)(1-\xi^2)P_l^{(m)} &= -(l+1-m)(l+2-m)P_{l+1}^{(m-1)}\\
&\quad + (l-1+m)(l+m)P_{l-1}^{(m-1)},
\end{aligned} \tag{31.20}$$

where $\xi = \cos\vartheta$. The deduction of these formulas is, in principle, quite simple [using, say, the defining equations (29.25)]; however, since it is somewhat long, and in any case of a purely formal character, we omit it here.

In order to find the matrix elements it is sufficient to rewrite the three expressions (31.20) by means of the normalized eigenfunctions (31.16), as

$$\begin{aligned}
(2l+1)\cos\vartheta\Phi_l^m &= \frac{N_{lm}}{N_{l+1m}}(l+1-m)\Phi_{l+1}^m + \frac{N_{lm}}{N_{l-1m}}(l+m)\Phi_{l-1}^m,\\
(2l+1)\sin\vartheta e^{i\varphi}\Phi_l^m &= \frac{N_{lm}}{N_{l+1m+1}}\Phi_{l+1}^{m+1} - \frac{N_{lm}}{N_{l-1m+1}}\Phi_{l-1}^{m+1},\\
(2l+1)\sin\vartheta e^{-i\varphi}\Phi_l^m &= -\frac{N_{lm}}{N_{l+1m-1}}(l+1-m)(l+2-m)\Phi_{l+1}^{m-1}\\
&\quad + \frac{N_{lm}}{N_{l-1m-1}}(l-1+m)(l+m)\Phi_{l-1}^{m-1}
\end{aligned} \tag{31.21}$$

for positive values of m. We need not consider separately the case of negative m, since the corresponding matrix elements may be deduced from those for positive m, by arguments of symmetry.

The matrix elements are essentially determined as coefficients of expansion from (31.21); the only remaining task is to calculate the ratios between the

N_{lm} by means of (31.19), thus finally arriving at

$$
\begin{aligned}
Z^{m\,m}_{l+1\,l} &= \left[\frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)}\right]^{1/2},\\
Z^{m\,m}_{l-1\,l} &= \left[\frac{(l+m)(l-m)}{(2l-1)(2l+1)}\right]^{1/2},\\
(X+iY)^{m+1\,m}_{l+1\,l} &= \left[\frac{(l+1+m)(l+2+m)}{(2l+1)(2l+3)}\right]^{1/2},\\
(X+iY)^{m+1\,m}_{l-1\,l} &= -\left[\frac{(l-m-1)(l-m)}{(2l-1)(2l+1)}\right]^{1/2},\\
(X-iY)^{m-1\,m}_{l+1\,l} &= -\left[\frac{(l+1-m)(l+2-m)}{(2l+1)(2l+3)}\right]^{1/2},\\
(X-iY)^{m-1\,m}_{l-1\,l} &= \left[\frac{(l-1+m)(l+m)}{(2l-1)(2l+1)}\right]^{1/2}.
\end{aligned}
\tag{31.22}
$$

Several of these elements may evidently be connected by changing the values of l and m; thus the latter three may, for instance, easily be obtained from the former three.

The main thing to note, however, is that these matrix elements furnish us with the important rules of selection and polarization with respect to transitions between the states of the system. The selection rules are

$$
m \to \begin{bmatrix} m+1 \\ m \\ m-1 \end{bmatrix}, \qquad l \to \begin{bmatrix} l+1 \\ l-1 \end{bmatrix},
\tag{31.23}
$$

or

$$
\Delta m = 0, \pm 1, \qquad \Delta l = \pm 1.
$$

Connection between the Dipole- and Momentum Matrix for a Rotator

Classically the radiation from an oscillating dipole may be determined by means of the dipole amplitude; however, we may also calculate it by using the amplitude for the momentum or acceleration. Hence we are not restricted to utilizing the dipole matrix only, when calculating transition probabilities; the elements of the momentum or acceleration matrix may also be employed.

The wave equation may also be used to determine the connection between the elements of these different matrices. We shall follow a similar procedure and deduce a set of matrix elements that are closely related to those in (31.22), but which actually correspond to the momentum matrix. This argument

will facilitate the subsequent purely matrix-mechanical treatment of such problems.

We introduce several auxiliary operators, closely related to the momentum operators p_x, and so forth, and gradient operators in (30.10); the auxiliary operators correspond to the latter multiplied by r (except for the r-component which vanishes for a rotator), that is, to the vector $r\nabla$. We denote the new operators by $\mathbf{P}$; the exact definition is

$$\begin{aligned}(P_x + iP_y) &= e^{i\varphi}\left\{\cos\vartheta\frac{\partial}{\partial\vartheta} - \frac{1}{\sin\vartheta}\frac{1}{i}\frac{\partial}{\partial\varphi}\right\},\\ (P_x - iP_y) &= e^{-i\varphi}\left\{\cos\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin\vartheta}\frac{1}{i}\frac{\partial}{\partial\varphi}\right\},\\ P_z &= -\sin\vartheta\frac{\partial}{\partial\vartheta}.\end{aligned} \tag{31.24}$$

Writing the three coordinate operators (31.17) together as a vector $\mathbf{R}$, it is clear that the vectors $\mathbf{P}$, $\mathbf{R}$, and $\mathbf{M}$ are orthogonal, connected by the equations

$$\mathbf{M} = \mathbf{r}\times\frac{1}{i}\nabla = \mathbf{R}\times\frac{1}{i}\mathbf{P}, \qquad \mathbf{P} = i\mathbf{M}\times\mathbf{R}. \tag{31.25}$$

Using the differential equation for the eigenfunctions

$$\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2} + l(l+1)\right]\Phi_l^{\,m} = 0 \tag{31.26}$$

we may show that

$$l\int_0^{\pi}\int_0^{2\pi}\Phi_{l+1}^{-m}\Phi_l^{\,m}\cos\vartheta\sin\vartheta\,d\vartheta\,d\varphi = \int_0^{\pi}\int_0^{2\pi}\Phi_{l+1}^{m}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\Phi_l^{\,m}\right)\sin\vartheta\,d\vartheta\,d\varphi \tag{31.27}$$

and another similar equation are valid; this implies, in turn, that

$$\begin{aligned}lZ_{ll+1}^{mm} &= -(P_z)_{l+1l}^{mm},\\ (l+1)Z_{l-1l}^{mm} &= (P_z)_{l-1l}^{mm}.\end{aligned} \tag{31.28}$$

Analogous formulas hold for the matrix elements of the remaining components of $\mathbf{R}$ and $\mathbf{P}$. However, the detailed mathematical treatment is rather involved, with several reformulations of integrals like that in (31.27) by means of (31.26) and subsequent partial integrations; the deduction of auxiliary formulas like those in (31.20) and (31.21) would, similarly, be quite tedious. We shall therefore omit such deductions, and instead rely wholly on the following matrix-mechanical considerations. This will also display the value of the

latter to more advantage. Even though matrix-mechanical lines of argument are often somewhat unwieldy to use, they deliver us from extensive analytical considerations of spherical functions. Such considerations are, on the other hand, quite simple in principle; however, they unavoidably become rather bulky.

Unfortunately the matrix-mechanical determination of coordinate- and momentum matrices for the free rotator is considerably more involved than that of the relatively simple spin matrix. We must imagine the angular momenta $\mathbf{M}^2$ and M_z to be quantized, and the main problem is then to find commutation relations between these quantities and the operators $\mathbf{R}$ and $\mathbf{P}$. For M_z, these relations are quite simple; the commutators are easily found, by means of the explicit expressions (31.17) and (31.24), to be

$$\begin{aligned} [M_z, X + iY] &= X + iY, & [M_z, P_x + iP_y] &= P_x + iP_y \\ [M_z, X - iY] &= -(X - iY), & [M_z, P_x - iP_y] &= -(P_x - iP_y), \\ [M_z, Z] &= 0, & [M_z, P_z] &= 0, \end{aligned} \tag{31.29}$$

This yields the well-known selection rules: $m \to (m+1), m, (m-1)$, which shows that all matrix elements with other combinations for the quantum number m vanish.

The commutators for $\mathbf{M}^2$ are somewhat more difficult to find; in particular, the expressions (31.17) and (31.24) are not very easy to use. For the P-operators, the commutation relations of which are the same as for the components of the ∇-operator, we may utilize the equations

$$\begin{aligned} \mathbf{M}^2 &= r^2 \nabla^2, \\ \left[\mathbf{M}^2, \frac{\partial}{\partial x}\right] &= \left[r^2, \frac{\partial}{\partial x}\right] \nabla^2 \\ &= -2x\nabla^2 = -2\frac{x}{r^2}\mathbf{M}^2 \end{aligned} \tag{31.30}$$

to obtain

$$[\mathbf{M}^2, P_x] = \mathbf{M}^2 P_x - P_x \mathbf{M}^2 = -2X\mathbf{M}^2. \tag{31.31}$$

The corresponding commutators for the coordinate matrices are

$$\mathbf{M}^2 X - X\mathbf{M}^2 = 2(X - P_x). \tag{31.32}$$

A simple way to prove this is to consider the commutator

$$[M_z, X] = iY \tag{31.33}$$

and cyclically corresponding expressions which follow from (31.29). We then

calculate the commutator $[\mathbf{M}^2, X]$ as follows:

$$\begin{aligned}
[M_x^2, X] &= 0, \\
[M_y^2, X] &= M_y[M_y, X] + [M_y, X]M_y = -i(M_yZ + ZM_y) \\
&= X - 2iM_yZ, \\
[M_z^2, X] &= M_z[M_z, X] + [M_z, X]M_z = i(M_zY + YM_z) \\
&= X + 2iM_zY, \\
[\mathbf{M}^2, X] &= 2X - 2i(M_yZ - M_zY) = 2(X - P_x).
\end{aligned} \tag{31.34}$$

As the next step we take the commutator of (31.34) with $\mathbf{M}^2$, obtaining

$$[\mathbf{M}^2, [\mathbf{M}^2, X]] = 2[\mathbf{M}^2, X] + 4X\mathbf{M}^2 \tag{31.35}$$

or

$$\mathbf{M}^4X - 2\mathbf{M}^2X\mathbf{M}^2 + X\mathbf{M}^4 - 2\mathbf{M}^2X - 2X\mathbf{M}^2 = 0. \tag{31.36}$$

Applying this operator to a state Φ_l, we find the equations

$$\begin{aligned}
X_{l'l}\{[l'(l'+1)]^2 - 2l'(l'+1)l(l+1) + [l(l+1)]^2 \\
- 2l'(l'+1) - 2l(l+1)\} = 0.
\end{aligned} \tag{31.37}$$

for the matrix elements $X_{l'l}$.

The condition for $X_{n'n} \neq 0$ is then that the expression in braces vanishes which yields the selection rules

$$l' = l + 1, \qquad l' = l - 1. \tag{31.38}$$

for all coordinates X, Y, Z. The same rules are valid for P_x, P_y, and P_z.

The commutation relations (31.31) or (31.34) now imply the validity of the hitherto unproved assertions in (31.28), namely,

$$\begin{aligned}
(P_x)_{l+1l} &= -lX_{l+1l}, \\
(P_x)_{l-1l} &= (l+1)X_{l-1l},
\end{aligned} \tag{31.39}$$

which also hold for P_y, Y, and P_z, Z.

By means of these equations we may now perform the following reformulation

$$\begin{aligned}
(2l+1)(2l+3)\,|Z_{l+1l}^{mm}|^2 &= (2l+3)Z_{ll+1}^{mm}(2l+1)Z_{l+1l}^{mm} \\
&= [(l+1)Z + P_z]_{ll+1}^{mm}[(l+1)Z - P_z]_{l+1l}^{mm} \\
&= \{[(l+1)Z + P_z][(l+1)Z - P_z]\}_{ll}^{mm}.
\end{aligned} \tag{31.40}$$

since by (31.39) the matrix elements

$$[(l+1)Z + P_z]_{l+2l+1}^{mm}, \qquad [(l+1)Z - P_z]_{l-1l}^{mm}$$

both vanish, so that the diagonal elements of the matrix (31.40) will consist

of a single product of two matrix elements. Utilizing (31.17) and (31.25), we apply the product operator (31.40) to Φ_l^m,

$$\left\{\left[(l+1)\cos\vartheta - \sin\vartheta\frac{\partial}{\partial\vartheta}\right]\cdot\left[(l+1)\cos\vartheta + \sin\vartheta\frac{\partial}{\partial\vartheta}\right]\right\}\Phi_l^m$$

$$= \left\{(l+1)^2 - \sin^2\vartheta\left[l(l+1) + \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin\vartheta\frac{\partial}{\partial\vartheta}\right]\right\}\Phi_l^m$$

$$= \{(l+1)^2 - m^2\}\Phi_l^m, \tag{31.41}$$

obtaining

$$|Z_{l+1l}^{mm}|^2 = \frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}. \tag{31.42}$$

A completely analogous procedure yields

$$\begin{aligned} |(X+iY)_{l+1l}^{m+1m}|^2 &= \frac{(l+1+m)(l+2+m)}{(2l+1)(2l+3)}, \\ |(X-iY)_{l+1l}^{m-1m}|^2 &= \frac{(l+1-m)(l+2-m)}{(2l+1)(2l+3)}. \end{aligned} \tag{31.43}$$

Thus we have determined the matrix elements (31.22) in a new and independent way, using no other analytical aids than the wave equation $\mathbf{M}^2\Phi_l^m = l(l+1)\Phi_l^m$ in (31.41).

32. TRANSITION PROBABILITIES IN THE HYDROGEN ATOM

Previously we have assumed that the emission or absorption of electromagnetic radiation from or by an atom in the course of a given quantum transition $n \to n'$, and with a fixed polarization direction x, y, or z, is proportional to the square modulus of the matrix elements $ex_{n'n}$, $ey_{n'n}$, $ez_{n'n}$. A satisfactory proof of this assumption may not be given until we have discussed the perturbation theory of stationary and nonstationary atomic systems.

Instead of $x_{n'n}$ and $y_{n'n}$, we shall employ the complex matrices $(x+iy)_{n'n}$ and $(x-iy)_{n'n}$, corresponding to right- and left-handed circularly polarized light for absorption, and vice versa for emission. This is easy to show by a more detailed formal discussion; however, we shall content ourselves with recalling that the two matrix elements correspond to the quantum transitions $m \to m+1$ and $m \to m-1$, that is, to an increase and a decrease, respectively, of the angular momentum of the atom with respect to the z-axis.

The possibility of thus referring the matrix elements and polarizations right away to a certain spatial direction arises from the fact that no spectral splitting of the polarized components occurs, except when we introduce an

external magnetic field to obtain a Zeeman effect. We shall always assume that any such magnetic field is in the z-direction.

We have the following relation between the matrix elements

$$|x_{n'n}|^2 + |y_{n'n}|^2 + |z_{n'n}|^2 = \tfrac{1}{2}[|(x + iy)_{n'n}|^2 + |(x - iy)_{n'n}|^2] + |z_{n'n}|^2. \tag{32.1}$$

Hence when calculating the intensities, we must always take care to include the factor $\frac{1}{2}$ in the complex matrix elements.

For the hydrogen atom with one single electron we have

$$x \pm iy = r \sin \vartheta e^{\pm i\varphi}, \qquad z = r \cos \vartheta. \tag{32.2}$$

The matrix elements may thus be expressed as follows

$$(x \pm iy)_{n'l'm'nlm} = r^{l'l}_{n'n}(X \pm iY)^{m'm}_{l'l}, \qquad z_{n'l'm'nlm} = r^{l'l}_{n'n}Z^{m'm}_{l'l}, \tag{32.3}$$

where

$$r^{l'l}_{n'n} = \int_0^\infty rR_{n'l'}R_{nl}r^2\,dr. \tag{32.4}$$

Here the R_{nl} represent normalized radial eigenfunctions and $l' = l \pm 1$; no selection rules exist for the transition $n \to n'$. The last factors in (32.3) are our previously found matrix elements for the free rotator, or generally for quantum transitions in the orbital spin of a particle.

Absorption and Emission for a Free Rotator with a Fixed Dipole Moment

Let us denote the fixed dipole moment of a free rotator by er_0, corresponding to, say, two charges e and $-e$ with the constant separation r_0, in contrast to the variable dipole moment er for an electron at a varying distance r from the atomic nucleus. This yields a constant factor $(er_0)^2$ for the square of the elements of the dipole matrix. For the moment we shall omit this factor in our considerations and discuss the dependence of the radiation on the quadratic matrix elements (31.43) and (31.22).

We may now proceed in two different ways. If the rotator is assumed to be in a given state $\Phi_l{}^m$, (31.43) will give us the probability for absorption. For right-hand circularly polarized light the absorption is then a maximum for $m = l$, that is, in the classical sense for a positive rotation about the z-axis. For left-hand circularly polarized light the maximum absorption occurs for the opposite rotation, that is, for $m = -l$. Linearly polarized light will be most strongly absorbed for $m = 0$, that is, for a rotation in a plane through the z-axis, classically speaking.

For nonpolarized radiation of the same intensity the absorption will be proportional to

$$\frac{1}{3}\left[\frac{1}{2}|(X+iY)^{m+1m}_{l+1l}|^2+\frac{1}{2}|(X-iY)^{m-1m}_{l+1l}|^2+|Z^{mm}_{l+1l}|^2\right]=\frac{l+1}{3(2l+1)} \tag{32.5}$$

for a single component.

When considering emission, we must utilize the corresponding quadratic matrix elements

$$\begin{aligned}|Z^{mm}_{l-1l}|^2&=\frac{l^2-m^2}{(2l-1)(2l+1)},\\ |(X-iY)^{m-1m}_{l-1l}|^2&=\frac{(l-1+m)(l+m)}{(2l-1)(2l+1)},\\ |(X+iY)^{m+1m}_{l-1l}|^2&=\frac{(l-1-m)(l-m)}{(2l-1)(2l+1)},\end{aligned} \tag{32.6}$$

which are given in (31.22) but may also be deduced without any difficulty from (31.43). The corresponding mean value of these is

$$\frac{(l-1)l+l^2}{3(2l-1)(2l+1)}=\frac{l}{3(2l+1)}. \tag{32.7}$$

The other procedure, which is more in accordance with the physical situation, is to accept that we do not know in which state the rotator is; hence we must assume a uniform statistical distribution of the rotator among the various states $-l \leqq m \leqq l$, in agreement with the correspondence principle. If we do not wish to adopt such as extreme point of view, we may choose to interpret the situation in such a way that a large number of rotators will distribute themselves uniformly among these states. With this starting point, we may calculate the mean value of the expressions (31.43) for $2l+1$ states $\Phi_l{}^m$, obtaining

$$\frac{1}{2}\overline{|(X+iY)^{m+1m}_{l+1l}|^2}=\frac{1}{2}\overline{|(X-iY)^{m+1m}_{l+1l}|^2}=\overline{|Z^{mm}_{l+1l}|^2}=\frac{l+1}{3(2l+1)}, \tag{32.8}$$

while the corresponding quantities for emission become

$$\frac{1}{2}\overline{|(X-iY)^{m-1m}_{l-1l}|^2}=\frac{1}{2}\overline{|(X+iY)^{m+1l}_{l-1l}|^2}=\overline{|Z^{mm}_{l+1l}|^2}=\frac{l}{3(2l+1)}. \tag{32.9}$$

Thus both the absorption and emission are independent of the polarization.

It is interesting to note that the absorption by (32.8) is strongest for the ground state, while the emission is zero for this state. The total emitted

radiation for all the three directions of polarization is proportional to

$$\frac{l}{2l+1}(er_0)^2 = 2\frac{2l}{2l+1}\left(\frac{er_0}{2}\right)^2. \tag{32.10}$$

Comparing this to the two oscillating dipoles

$$\begin{aligned} x &= r_0 \cos \omega t = \frac{r_0}{2}(e^{i\omega t} + e^{-i\omega t}), \\ y &= r_0 \sin \omega t = \frac{r_0}{2i}(e^{i\omega t} - e^{-i\omega t}), \end{aligned} \tag{32.11}$$

resulting from a rotation of the rotator in the xy-plane, the correspondence between the classical and quantum-theoretical laws of radiation becomes immediately evident. The factor $\frac{1}{2}$, which by our definitions appears in the matrix elements, is compensated in the expression for radiation intensity by a factor four, compared with the classical radiation formula.

Emission and Absorption in an Atom

The quantum transitions or "jumps" of an electron in an atom are rather similar to the transitions for a free rotator, as far as the change in the spin is concerned. The electrical dipole moment of the atom is, however, of a character quite different from that of the rotator: the latter must, as already mentioned, be thought of as having a fixed dipole moment; the time-dependent variation of the components of the dipole moment in a fixed coordinate system is then due to the motion of the rotator.

In an atom we must regard the dipole moment as time-dependent and due to a combination of two quantum states of different energies. The amplitude for this dipole moment may be measured by the radial part $er_{n'n}^{l'l}$ of the matrix element, which replaces the dipole moment $er_0/2$ for the rotator.

The rotational energy is of secondary importance in an atom. To be more precise, by introduction of the principal quantum number $n = n_r + l + 1$, this energy is included (together with the radial kinetic energy) in a total energy quantity which depends mainly on this quantum number; thus, for instance, $E = -Rh/n^2$ for the hydrogen atom. Hence since the change of energy is chiefly connected with changes in the principal quantum number, increases or decreases of the azimuthal quantum number are no longer decisive for the question of absorption or emission. The transitions $l \to l+1$ and $l \to l-1$ will both be included in the emission, and also in the absorption. Disregarding for the moment spontaneous emission of radiation, so that we need not define an external radiation field, the single components of the polarized radiation will contribute the fractions

$$\frac{l+1}{3(2l+1)}, \qquad \frac{l}{3(2l+1)},$$

and all three components together the fractions

$$\frac{l+1}{2l+1} + \frac{l}{2l+1} = 1 \tag{32.12}$$

of the total emitted radiation, for the transitions

$$l \to l+1, \qquad l \to l-1,$$

respectively.

Calculation of the Mean Values of r for the Hydrogen Atom

The experimental study of the absolute radiation intensity from an atom is very difficult, and even relative measurements of the intensity of spectral lines with a common upper or lower energy term involve rather complicated observational procedures. For this reason the calculation of matrix elements and transition probabilities has not been of such immediate practical interest as that of energy levels or spectral terms. From the theoretical point of view, however, the matrix elements and transition probabilities are of no less interest than the energy levels, and are often of great importance for advanced theoretical deductions. The main reason why we include the calculation of the radial matrix elements for the hydrogen atom, however, is that they furnish an interesting basis for comparison with the corresponding quantities which we have deduced, by means of the correspondence principle, from the earlier quantum theory.

Since the calculation of matrix elements is a purely formal and technical problem, we shall employ the presumably most "rapid" method, namely, the definition of the Laguerre polynomials and their derivatives by means of generating functions. The complete formal deduction is somewhat involved and will not be given in too great detail here; the main thing is the method and the results. To facilitate the exposition we shall first calculate the mean values of positive and negative powers of r, which may be done in a fairly easy way.

The Laguerre polynomials

$$L_0(x) = 1,\ L_1(x) = 1 - x, \cdots, L_n(x) = n! - \cdots + (-1)^n x^n \tag{32.13}$$

may be defined by the formula

$$L_n(x) = e^x \frac{d^n}{dx^n}(x^n e^{-x}) \tag{32.14}$$

or by means of a generating function

$$\psi(x, s) = \frac{\exp\left[-(xs/1-s)\right]}{1-s} = \sum_{n=0}^{\infty} \frac{L_n(x)}{n!} s^n. \tag{32.15}$$

Consequently the Laguerre polynomials L_{n+1}^{2l+1}, which appear in the hydrogen eigenfunctions, are expressible by the equation

$$\Psi(x, s) = -\frac{\exp[-(sx/1-s)]}{(1-s)^{2l+2}} = \sum_{n=l+1}^{\infty} \frac{L_{n+l}^{2l+1}(x)}{(n+l)!} s^{n-l-1}. \tag{32.16}$$

We now write the hydrogen eigenfunctions in the form

$$R_{nl}(r) = -N_{nl} e^{-(\rho/2n)} \left(\frac{\rho}{n}\right)^l \frac{L_{n+l}^{2l+1}(\rho/n)}{(n+l)!}, \tag{32.17}$$

where

$$\rho = \frac{2r}{a_H}, \qquad r = \rho \frac{a_H}{2}, \qquad a_H = \frac{h^2}{4\pi^2 me^2} \tag{32.18}$$

and

$$N_{nl} = \left[\frac{(n-l-1)!}{2n^4(n+l)!}\right]^{1/2} \tag{32.19}$$

is a factor of normalization. It is then possible to define the radial eigenfunctions by means of a generating function

$$\psi_l\left(\frac{\rho}{n}, s\right) = \frac{\exp[-(\rho/2n)(1+s/1-s)]}{(1-s)^{2l+2}} \left(\frac{\rho}{n}\right)^l, \tag{32.20}$$

that is, as the coefficient of s^{n-l-1} in the expansion of ψ_l in powers of s. Since n appears both in ψ_l and as an exponent in the power to be determined, we shall prefer to express the eigenfunction to be found by means of a contour integral around the origin in the complex s-plane,

$$R_{nl}(\rho) = N_{nl} \frac{1}{2\pi i} \oint \frac{ds}{s^{n-l}} \psi_l\left(\frac{\rho}{n}, s\right). \tag{32.21}$$

Since

$$\int_0^\infty \psi_l\left(\frac{\rho}{n}, s\right)\psi_l\left(\frac{\rho}{n}, t\right)\rho^2 \, d\rho = n^3 \frac{(2l+2)!\,(1-s)(1-t)}{(1-st)^{2l+3}}$$

$$= n^3 \sum_k \frac{(2l+2+k)!}{k!}(1-s)(1-t)s^k t^k, \tag{32.22}$$

we easily find that

$$\int_0^\infty [R_{nl}(\rho)]^2 \rho^2 \, d\rho = N_{nl}^2 \frac{2n^4(n+l)!}{(n-l-1)!} = 1. \tag{32.23}$$

Thus the eigenfunctions are normalized with respect to the independent variable ρ instead of r.

When calculating $\bar{\rho}$, $\overline{\rho^{-1}}$, $\overline{\rho^{-2}}$, we obtain

$$n^4 \frac{(2l+3)!\,(1-s)^2(1-t)^2}{(1-st)^{2l+4}} = n^4 \sum_k \frac{(2l+3+k)!}{k!} s^k t^k (1-s)^2(1-t)^2,$$

$$n^2 \frac{(2l+1)!}{(1-st)^{2l+2}} = n^2 \sum_k \frac{(2l+1+k)!}{k!} s^k t^k,$$

$$n \frac{(2l)!}{(1-st)^{2l+1}(1-s)(1-t)} = \frac{n}{2l+1} \sum_k \frac{(2l+1+k)!}{k!} s^k t^k \frac{1-st}{(1-s)(1-t)},$$

by solving integrals corresponding to (32.22). Considering the terms $s^{n-l-1}t^{n-l-1}$, this yields the mean values

$$\begin{aligned} \bar{\rho} &= 3n^2 + l(l+1), \\ \overline{\rho^{-1}} &= \frac{1}{2n^2}, \\ \overline{\rho^{-2}} &= \frac{1}{2n^3(2l+1)}. \end{aligned} \tag{32.24}$$

The determination of mean values of higher and lower powers turns out to be considerably more difficult, when this procedure is used. One may, however, obtain a useful recursive formula by multiplying the differential equation for $R_{nl}(\rho)$ by

$$(m-1)\rho^{m+2}R_{nl} - 2\rho^{m+3}R'_{nl}$$

and integrating from $\rho = 0$ to $\rho = \infty$; this yields

$$(m+1)\overline{\rho^m} - 2n^2(2m+1)\overline{\rho^{m-1}} + n^2 m[(2l+1)^2 - m^2]\overline{\rho^{m-2}} = 0. \tag{32.25}$$

Using the fact that $\overline{\rho^0} = 1$, this formula may be employed to calculate the mean values of ρ^{-1}, ρ, ρ^2, $\cdots$; for the determination of the mean values of ρ^{-3}, ρ^{-4}, $\cdots$, however, one needs to know $\overline{\rho^{-2}}$.

If we now calculate the mean values of powers of

$$r = \rho \frac{a_H}{2},$$

and introduce the quantity

$$a = n^2 a_H \tag{32.26}$$

corresponding to the major semiaxis of a classical elliptic orbit with the same

energy, we obtain

$$\bar{r} = a\left(\frac{3}{2} + \frac{l(l+1)}{2n^2}\right), \qquad \overline{r^{-1}} = \frac{1}{a},$$

$$\overline{r^2} = a^2\left(\frac{5}{2} + \frac{3}{2}\frac{l(l+1) - \frac{1}{3}}{n^2}\right), \qquad \overline{r^{-2}} = \frac{1}{a^2}\frac{n}{l+\frac{1}{2}}, \tag{32.27}$$

$$\overline{r^{-3}} = \frac{1}{a^3}\frac{n^3}{l(l+\frac{1}{2})(l+1)}.$$

The derivation from the corresponding mean values in Bohr's theory was discussed earlier.

Calculation of Radial Matrix Elements

The calculation of the radial matrix elements is considerably more difficult. We obtain expressions for these in the form of terminating series which may become extremely unwieldy if one does not succeed in finding the most suitable form. A great simplification results if we first of all, using the differential equations for R_{nl} and $R_{n'l+1}$, reformulate the matrix elements as follows

$$r_{n'n}^{l+1\,l} = \frac{a_H}{2}\int_0^\infty R_{n'l+1}R_{nl}\rho^3\,d\rho$$

$$= \frac{4n^2n'^2}{n^2 - n'^2}\,a_H\int_0^\infty R_{n'l+1}\rho^{l+2}\frac{d}{d\rho}\,\rho^{-l}R_{nl}\,d\rho. \tag{32.28}$$

The calculus of (32.28) is elementary and will not be discussed in any detail here. For the case $n = n'$, which may be treated in a very simple way, we shall content ourselves with stating the result

$$r_{nn}^{l+1\,l} = -\tfrac{3}{2}a_H n[n^2 - (l+1)^2]^{1/2} = -\tfrac{3}{2}a\varepsilon, \qquad \varepsilon = [1 - (l+1)^2/n^2]^{1/2}. \tag{32.29}$$

This will be seen to correspond completely to the result we found when studying the elliptic orbits of Bohr if we replace the "half-integral" azimuthal quantum numbers $l + \frac{1}{2}$ and $l + \frac{3}{2}$ for the two orbits by their arithmetic mean $l + 1$. We note the value of the "eccentricity" ε, as stated in (32.29).

Now calculating the integral

$$\int_0^\infty \psi_{l+1}\left(\frac{\rho}{n'}, t\right)\rho^{l+2}\frac{d}{d\rho}\,\psi_l\left(\frac{\rho}{n}, s\right)d\rho,$$

and ordering the result, we obtain

$$r_{n'n}^{l+1\,l} = \frac{a_H}{4}\frac{(nn')^{l+3}}{[(n+n')/2]^{2l+6}}\cdot\frac{n'+n}{n'-n}\cdot\frac{1}{2\pi i}\oint\frac{ds}{s^{n-l}}\frac{1}{2\pi i}\oint\frac{dt}{t^{n'-l-1}}$$

$$\cdot\left[\frac{(n-l-1)!\,(n'-l-2)!}{(n+l)!\,(n+l+1)!}\right]^{1/2}\frac{(2l+1)!\,(1-s^2)}{\{1 - st + [(n'-n)/(n'+n)](s-t)\}^{2l+4}}. \tag{32.30}$$

Here we may expand, first in powers of $(s - t)$ and then in powers of st; this yields for $n' > n$ and $n > n'$ two apparently different formulas; however, one may pass from one to the other and back again by changing the index of summation k to $n' - n + k$, and vice versa. The two formulas are

$$r_{n'n}^{l+1\,l} = \frac{a_H}{4}\frac{(nn')^{l+3}}{[(n+n')/2]^{2l+6}}\left[\frac{(n-l-1)!\,(n'-l-2)!}{(n+l)!\,(n'+l+1)!}\right]^{1/2}\cdot\begin{cases}F, & n'>n,\\ G, & n>n',\end{cases}$$

$$F = \sum_{k=0}^{n-l-1}(-1)^k\left(\frac{n'-n}{n'+n}\right)^{n'-n-2+2k}$$

$$\cdot\left[\frac{(n'+l+1+k)!}{(n'-n-1+k)!\,k!\,(n-l-1-k)!} + \frac{(n'+l+k)!}{(n'-n+k)!\,(k-1)(n-l-2-k)!}\right], \tag{32.31}$$

$$G = \sum_{k=0}^{n'-l-1}(-1)^k\left(\frac{n-n'}{n+n'}\right)^{n-n'-2+2k}$$

$$\cdot\left[\frac{(n+l+1+k)!}{(k-1)!\,(n-n'+k)!\,(n'-l-1-k)!} + \frac{(n+l+k)!}{k!\,(n-n'-1+k)!\,(n'-l-2+k)!}\right].$$

For transitions corresponding to observed spectral lines, these series contain only a few terms. We are, however, more interested in the correspondence with the "matrix elements" or intensity (Fourier) coefficients; hence we consider the limiting case—of no importance for practical purposes, but of great interest theoretically—when both n and n' approach ∞, while $\Delta n = |n' - n|$ remains finite.

Introducing

$$a = a_H\left(\frac{n'+n}{2}\right)^2, \qquad \varepsilon^2 = 1 - \frac{(l+1)^2}{[(n+n')/2]^2}, \qquad \Delta n = \nu, \tag{32.32}$$

we shall, when l is also a large number, obtain a fairly good approximation to the two formulas (32.21) if we replace them by

$$r_{n'n}^{l+1\,l} = \frac{a}{\nu^2}\sum_{k=0}^{\infty}(-1)^k\left(\frac{\varepsilon\nu}{2}\right)^{\nu+2k}\cdot\left[\frac{1}{k!\,(\nu-1+k)!} + \frac{1}{(k-1)!\,(\nu+k)!}\right]. \tag{32.33}$$

This is because the series converges very rapidly for moderate values of ν, so that we may take $k \ll l$. This series may also be written

$$r_{n'n}^{l+1\,l} = \frac{\varepsilon a}{\nu}J_\nu{}'(\varepsilon\nu), \tag{32.34}$$

where $J_\nu(x)$ is the νth-order Bessel function.

As found previously, in Chapter 2, (22.21), this is just the $\nu = |n' - n|$-th Fourier coefficient for the radial distance of an electron from the focal point, when it moves in an elliptic orbit with the major semiaxis a and eccentricity ε.

33. THE ZEEMAN EFFECT AND THE ELECTRON SPIN

The Normal Zeeman Effect

We have previously seen that the Hamiltonian takes the form

$$H = \frac{1}{2m_0}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 + V - e\varphi, \tag{33.1}$$

when an electron with the charge $(-e)$ moves in an electromagnetic field with the scalar and vector potentials φ and $\mathbf{A}$. The quantity $-e\varphi$ may, if we like, be included in the potential energy V; this is actually what we have done before with the potential energy of the Coulomb field, where the vector potential $\mathbf{A}$ vanishes and where the potential energy is just the quantity $-e\varphi$ in (33.1).

We will now consider an electromagnetic field which, in addition to the electrostatic Coulomb potential, contains a rectilinear homogeneous magnetic field $\mathbf{H} = H_z\mathbf{k}$ in the z-direction. This field may be derived from a divergence-free vector potential

$$\mathbf{A} = \tfrac{1}{2}H_z(-y\mathbf{i} + x\mathbf{j}) \tag{33.2}$$

by the equation

$$\mathbf{H} = \operatorname{curl}\mathbf{A}. \tag{33.3}$$

In general (33.1) will give rise to some lesser complications, since the order of $\mathbf{p}$ and $\mathbf{A}$ in the product terms must be taken into account; furthermore the quadratic term in $\mathbf{A}$ may cause some difficulties. For the homogeneous field (33.2) the first of these complications does not appear, and the quadratic term in $\mathbf{A}$ will (as is very often done) be omitted here, since it represents higher-order effects of secondary importance. The product term in (33.1) will, for the field (33.2), take the form

$$\frac{eH_z}{2m_0c}(xp_y - yp_x) = \frac{eH_z}{2m_0c}p_\varphi = \frac{eh}{4\pi m_0 c}H_z\frac{1}{i}\frac{\partial}{\partial\varphi}. \tag{33.4}$$

With these simplifications the wave equation for a hydrogen atom in a homogeneous magnetic field will then read

$$H\psi = \left[\frac{1}{2m_0}\left(\frac{h}{2\pi i}\right)^2\nabla^2 + \frac{eh}{4\pi m_0 c}H_z\frac{1}{i}\frac{\partial}{\partial\varphi} - \frac{e^2}{r}\right]\psi = E\psi. \tag{33.5}$$

We now imagine that the motion is quantized with respect to angular

momentum and energy, and write

$$\psi = R_{nl}(r)P_l^m(\cos\vartheta)e^{im\varphi}. \tag{33.6}$$

The additional energy due to the magnetic field is then the eigenvalue of the operator

$$\mu_0 H \frac{1}{i}\frac{\partial}{\partial\varphi},$$

that is,

$$E_m = m\mu_0 H_z, \qquad \mu_0 = \frac{eh}{4\pi m_0 c}, \tag{33.7}$$

where the quantity μ_0 is called a Bohr magneton. We say that the atom has, in this state, a magnetic moment $m\mu_0$ in the direction of the field (actually it is $-m\mu_0$ because of the negative charge of the electron).

This Zeeman effect in the splitting of the energy levels will, to a great extent, not be observed in the spectral lines due to the selection rules. The spectral line shift does not depend on m. On the other hand, a difference will appear because of the three selection rules; this may be expressed as follows:

$$\begin{aligned} \Delta\nu &= \nu_0 = \frac{eH_z}{4\pi m_0 c} && \text{for } m \to m-1, \\ \Delta\nu &= -\nu_0 = -\frac{eH_z}{4\pi m_0 c} && \text{for } m \to m+1, \\ \Delta\nu &= 0 && \text{for } m \to m. \end{aligned} \tag{33.8}$$

This is the "normal" Zeeman effect for a spectral line; the three expressions (33.8) correspond, in the given order, to right- and left-hand circularly polarized light and to linearly polarized light (with respect to the z-axis).

On a closer examination we find that this is in complete agreement with Lorentz' theory of the Zeeman effect. The right-hand polarized light corresponds to a positive sense of revolution by the electron about the positive z-axis. The Lorentz force will then, for a negatively charged electron, point inward toward the center of the orbit (compare Fig. 4-2); hence the period

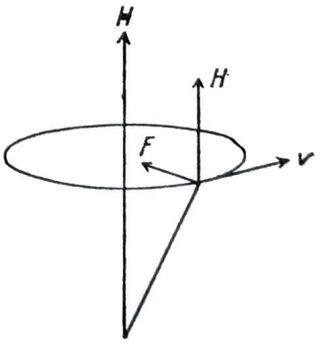

Fig. 4-2. Explanation of the Zeeman effect.

of revolution must increase if the centrifugal force is to balance the inward-pointing force.

The Anomalous Zeeman Effect

The normal Zeeman effect is rarely observed—as a matter of fact, only for the so-called singlet terms, such as parahelium (symmetric states) where the spins of the two electrons are antiparallel. For one electron, as in the hydrogen atom, we have so-called doublet terms which show an "anomalous" Zeeman effect. Let us see how this occurs.

The ratio of the magnetic moment of the spinning electron to its intrinsic spin is, as already mentioned in (19.26), twice as large as the corresponding ratio between the magnetic moment and mechanical angular momentum of the electronic orbit. Let us once again denote the orbital and intrinsic spins in the unit $h/2\pi$, by $\mathbf{M}$ and $\mathbf{S}$. In analogy with (33.4) we may then put the additional magnetic energy of the atom equal to

$$E_m = \mu_0 H_z(M_z + 2S_z). \tag{33.9}$$

We now run into difficulties, since this quantity may not be quantized. According to general rules, which apply to all compound angular momenta, we must assume that it is the total spin $\mathbf{M} + \mathbf{S}$ that is a constant of the motion; this will be proved to hold in Dirac's relativistic electron theory. In (33.9) it is thus the quantity

$$m_z = M_z + S_z \tag{33.10}$$

that signifies the "normal" part of the Zeeman effect, while the remainder S_z denotes the deviation from it. (The term $\mathbf{m}$ is here introduced as a preliminary notation for the total spin.)

For weak magnetic fields, it turns out that the electron spin exhibits a relatively rapid precession about the total spin, so that we need only consider the component of electron spin along the total spin. Thus we may write

$$S_z = m_z \frac{\mathbf{mS}}{\mathbf{m}^2} \tag{33.11}$$

or, since $\mathbf{m} = \mathbf{M} + \mathbf{S}$, $\mathbf{M} = \mathbf{m} - \mathbf{S}$,

$$S_z = m_z \frac{\mathbf{m}^2 + \mathbf{S}^2 - \mathbf{M}^2}{2\mathbf{m}^2}. \tag{33.12}$$

We now put

$$\mathbf{m}^2 = j(j+1), \qquad \mathbf{S}^2 = s(s+1), \qquad \mathbf{M}^2 = l(l+1), \tag{33.13}$$

where j is the quantum number for the total spin, $j = l \pm \frac{1}{2}$, since $s = \frac{1}{2}$ for a

single electron. Writing $m_s = m_j$, we obtain the splitting

$$E_m = \mu_0 H_z m_j \left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}\right], \qquad (33.14)$$

$$m_j = -j, -j+1, \cdots, j-1, j.$$

of the terms.

This expression, commonly referred to as Landé's formula, must evidently hold also for the addition of orbital and intrinsic spins of several electrons; this has been verified by the study of the anomalous Zeeman effects exhibited by several different types of atoms. We must then only allow for the different possibilities for the total spin quantum numbers of the electrons

$$s = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \cdots, \qquad (33.15)$$

corresponding to the different multiplet terms, and also for the different possibilities for the total spin

$$j = |l - s|, |l - s| + 1, \cdots, l + s. \qquad (33.16)$$

34. THE SPLITTING OF TERMS FOR ATOMS CONTAINING SEVERAL ELECTRONS

The Dependence of the Energy Terms on the Azimuthal Quantum Number

It is only for the hydrogen atom with one single electron, and for the homologous ions He^+, Li^{++}, and so forth, that the energy terms depend solely on the principal quantum number. In other atoms we shall also have one single electron, the "light-electron," playing the leading role in the formation of the optical spectra. However, this electron will be in a more complicated force field, which will give rise to a splitting of the energy terms, depending on the azimuthal quantum number $l = 0, 1, 2, \cdots$, and so forth, into states which we denote as S-, P-, D-states, and so on. Strictly speaking, we cannot treat the force field acting on one of the outer electrons as constant, since it will depend on the state of motion of the other electrons. On the average, however, we may—to a fairly satisfactory degree of accuracy—think of the Coulomb field Ze/r from the nuclear charge as being more or less effectively "screened down" to a field e/r. In addition to this field we must consider certain corrective terms, decreasing more rapidly than $1/r$ with the radial distance r; these will then give rise to a shift of the energy levels as compared with the corresponding hydrogen terms. This shift has its maximum value for the S-states, $l = 0$, where the electron is, on the average, closer to the nucleus than in the other states. For increasing l, the terms become more and more "hydrogen-like."

We shall here content ourselves with giving a qualitative picture of the

splitting of terms by means of a very drastically simplified description of the atomic force field, namely, by expressing the deviation from the Coulomb potential as an addition potential energy term of the form $1/r^2$. Such a term has the important property of decreasing considerably more rapidly than the Coulomb term. For small r, however, it corresponds rather poorly to the physical reality; nevertheless, it will at least give a deviation in the right direction, even in this case.

We write the force field acting on the electron as

$$V = -\frac{e^2}{r} - \frac{h^2}{8\pi^2 m_0}\frac{g}{r^2}, \tag{34.1}$$

where the last term is the correction mentioned above. This yields the radial wave equation

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)-g}{r^2} + \frac{8\pi^2 m_0}{h^2}\left(E + \frac{e^2}{r}\right)\right]R_{nl} = 0. \tag{34.2}$$

For the numerator in the r^{-2}-term, we put

$$\begin{gathered} l(l+1) - g = \lambda(\lambda+1), \\ \lambda = -\frac{1}{2} + \left[\left(l+\frac{1}{2}\right)^2 - g\right]^{1/2} \approx l - \frac{g}{2l+1}. \end{gathered} \tag{34.3}$$

The equation (34.2) is in principle just as easy to solve as the radial wave equation for the Kepler problem. We shall not investigate this problem any further here, but only state that the exact eigenvalue is

$$E_{nl} = -\frac{Rh}{(n_r+\lambda+1)^2} = -\frac{Rh}{(n+\lambda-l)^2} = -\frac{Rh}{(n-\delta)^2}, \tag{34.4}$$

where $n = n_r + l + 1$ is the principal quantum number. The corresponding Rydberg correction is

$$\delta \approx \frac{g}{2l+1}. \tag{34.5}$$

It clearly becomes rather small for large l, and is in reasonable qualitative agreement with the Rydberg corrections determined experimentally for corresponding S-, P-, and D-states of an atomic electron.

In the previous sections we have been able to give an exact wave-mechanical treatment of one-electron systems only; however, the considerations of the present section give us some idea of the states of electrons, even in more complicated atomic systems. Further progress in the treatment of such problems must be deferred until we have studied the theory of perturbation for systems containing several electrons. In the meantime, we shall now complete our discussion of electron spin and other relativistic effects by a presentation of Dirac's relativistic electron theory.

CHAPTER 5

Relativistic Quantum Theory

35. THE RELATIVISTIC WAVE EQUATION

The Hamiltonian in Relativity Theory

Before formulating a relativistic wave equation we shall recapitulate briefly some facts concerning equations of motion and energy functions in relativity theory. Previously we have found that the relativistic equations of motion for a particle, with or without an electromagnetic field, may be written in the Lagrangian formulation

$$p_x = \frac{\partial L}{\partial \dot{x}}, \qquad \dot{p}_x = \frac{\partial L}{\partial x}. \tag{35.1}$$

For an electron with the charge $(-e)$ the Lagrangian function $L(x, \dot{x})$ must then have the form

$$L = -m_0 c^2 \left(1 - \frac{v^2}{c^2}\right)^{1/2} - \frac{e}{c}\mathbf{vA} + e\Phi. \tag{35.2}$$

Here m_0 is the mass of the electron, $\mathbf{v} = \dot{x}\mathbf{i} + \dot{y}\mathbf{j} + \dot{z}\mathbf{h}$ its velocity, and $\mathbf{A}$ and Φ the vector and scalar potential of the electromagnetic field.

This leads to the following expressions for the Cartesian components of momentum,

$$p_x = \frac{m_0 \dot{x}}{(1 - \beta^2)^{1/2}} - \frac{e}{c} A_x, \qquad \beta = \frac{v}{c}. \tag{35.3}$$

The energy function, by means of which we may write the equations of motion in the Hamiltonian formulation

$$\dot{x} = \frac{\partial H}{\partial p_x}, \qquad \dot{p}_x = -\frac{\partial H}{\partial x}, \tag{35.4}$$

is then, as usual, given by

$$\begin{aligned} H &= \dot{x}p_x + \dot{y}p_y + \dot{z}p_z - L \\ &= \frac{m_0 c^2}{(1 - \beta^2)^{1/2}} - e\Phi. \end{aligned} \tag{35.5}$$

This is not, however, the correct Hamiltonian, since the latter must be a function of coordinates and momenta. This function may be obtained by elimination of $\dot{x}$, $\dot{y}$, and $\dot{z}$, using (35.3); it is commonly formulated as

$$\frac{H}{c} = \left[\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 + m_0^2c^2\right]^{1/2} - \frac{e}{c}\Phi. \tag{35.6}$$

It may, however, be instructive to note a form intermediate between (35.5) and (35.6), namely,

$$\frac{H}{c} = \frac{\dot{x}}{c}\left(p_x + \frac{e}{c}A_x\right) + \frac{\dot{y}}{c}\left(p_y + \frac{e}{c}A_y\right) + \frac{\dot{z}}{c}\left(p_z + \frac{e}{c}A_z\right) + \left(1 - \frac{v^2}{c^2}\right)^{1/2} m_0c - \frac{e}{c}\Phi. \tag{35.7}$$

The Relativistic Wave Equation for a Free Electron

The greatest difficulty encountered in the consideration of a Hamiltonian of the form (35.6), from the wave-mechanical point of view, is that we may not right away replace the momenta by differential operators, since they appear in a square root. One has tried to avoid this difficulty by considering the function $(H + e\Phi)^2$, thus apparently "eliminating" the square root sign. However, this procedure runs into conflict with the commutation rules for momenta and coordinates; hence it is bound to yield erroneous results for effects of a relativistic order of magnitude. This becomes apparent when the fine-structure formula for the hydrogen atom and hydrogen-like ions is deduced. We shall not, therefore, discuss this obsolete procedure here.

However, if we consider the Hamiltonian for a free particle

$$\frac{H}{c} = (p_x^2 + p_y^2 + p_z^2 + m_0^2c^2)^{1/2}, \tag{35.8}$$

which depends only on the momenta, these commutation difficulties do not arise. We may apply the operator twice, thus eliminating the square root sign, and then assign to the momenta the usual significance of differential operators. In this way we may even determine wave functions for the particle in the form

$$\psi = \exp\left[\frac{2\pi i}{h}(p_x'x + p_y'y + p_z'z\right] \tag{35.9}$$

where p_x', and so forth, are eigenvalues for the momenta. This does not, however, yield any direct general wave-mechanical definition of the operator (35.8).

We shall now show that this energy operator for a free particle may be written in a different way, which corresponds to the only significance we can assign to the operator (35.8) at this stage:

$$\left(\frac{H}{c}\right)^2 = p_x^2 + p_y^2 + p_z^2 + m_0^2 c^2. \tag{35.10}$$

The new operator will be given a rational form which allows us to maintain the interpretation of momenta as differential operators.

We write

$$\frac{H}{c} = \alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z + \alpha_4 m_0 c. \tag{35.11}$$

Concerning the new operators α we shall at this stage assume only that they commute with the momenta. In order that (35.10) be satisfied we must then require that

$$\begin{gathered} \alpha_1^2 = \alpha_2^2 = \alpha_3^2 = \alpha_4^2 = 1, \\ \alpha_1\alpha_2 + \alpha_2\alpha_1 = 0, \cdots, \alpha_3\alpha_4 + \alpha_4\alpha_3 = 0, \end{gathered} \tag{35.12}$$

or, in general,

$$\alpha_i\alpha_k + \alpha_k\alpha_i = 2\delta_{ik}. \tag{35.13}$$

The α_k hence constitute a set of normalized *anticommutative* operators, similar to the previously mentioned spin matrices σ_1, σ_2, σ_3.

Anticommutative Operators and Hypercomplex Numbers

In his book *Atombau und Spektrallinien II*, A. Sommerfeld has introduced an interesting method of discussing operators of the kind displayed above, namely, by treating them as hypercomplex numbers. We shall not make use of this method in any detail; nevertheless, we give a short presentation of it for the reader to realize that the matrix representation of the α-operators is not fundamental or essential.

Let us, to begin with, consider a set of three anticommuting operators which we denote by ρ_1, ρ_2, ρ_3. From these we may form new product operators in altogether eight different ways, which we order as follows

$$\begin{gathered} \rho_1 \quad \rho_2 \quad \rho_3 \quad 1, \\ \frac{1}{i}\{\rho_2\rho_3 \quad \rho_3\rho_1 \quad \rho_1\rho_2 \quad \rho_1\rho_2\rho_3\}. \end{gathered} \tag{35.14}$$

This is the maximum number; as soon as we introduce other products the number of independent terms will be decreased by equations, such as

$$\rho_1\rho_2 = -\rho_2\rho_1\,, \quad \rho_1^2 = 1.$$

In the last four operators (35.14) we have inserted the factor i^{-1}; these will then also have squares equal to unity. The operators in the two rows (35.14)

are completely equivalent and may evidently be identified with the previously considered spin operators, σ_1, σ_2, σ_3, and the unit operator 1, all of which are representable by two-dimensional matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \qquad 1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{35.15}$$

If we consider four mutually anticommutative operators γ_1, γ_2, γ_3, γ_4, with squares equal to unity, the operation becomes more complicated. We then obtain altogether 16 product operators which may be ordered as follows

$$\begin{array}{cccc} \gamma_1 & \gamma_2 & \gamma_3 & \gamma_4, \\ \frac{1}{i}\{\gamma_4\gamma_1 & \gamma_4\gamma_2 & \gamma_4\gamma_3 & \gamma_1\gamma_2\gamma_3\}, \\ \frac{1}{i}\{\gamma_2\gamma_3\gamma_4 & \gamma_3\gamma_1\gamma_4 & \gamma_1\gamma_2\gamma_4\} & \gamma_1\gamma_2\gamma_3\gamma_4, \\ \gamma_3\gamma_2 & \gamma_1\gamma_3 & \gamma_2\gamma_1 & 1. \end{array} \tag{35.16}$$

The operators in the first three rows each constitute a set of equivalent anticommuting operators with squares unity; in the last row only the first three operators anticommute, while (of course) the unit operator 1 *commutes* with all operators. In passing we note that these last four operators are of some interest, in that they are equivalent to the so-called *quaternion group*. For this reason we have abstained from normalizing them in the usual way and have also chosen the order $3-2, 1-3, 2-1$ instead of $2-3, 3-1, 1-2$. Denoting these operators in the above order as

$$i \quad j \quad k \quad 1,$$

we obtain the following relations

$$\begin{aligned} i^2 = j^2 = k^2 &= -1, \\ jk = -kj &= i, \\ ki = -ik &= j, \\ ij = -ji &= k. \end{aligned} \tag{35.17}$$

We shall now consider the problem from a different point of view and attempt to determine a set of nine anticommuting operators by means of a double set of operators of the type σ_1, σ_2, σ_3; we denote the second set by ρ_1, ρ_2, ρ_3, and assume that they commute with the σ-operators. The quantities

$$\gamma_1 = \rho_1\sigma_1, \qquad \gamma_2 = \rho_1\sigma_2, \qquad \gamma_3 = \rho_1\sigma_3, \qquad \gamma_4 = \rho_3, \tag{35.18}$$

where

$$\sigma_1\sigma_2 = -\sigma_2\sigma_1 = i\sigma_3, \qquad \rho_1\rho_2 = -\rho_2\rho_1 = i\rho_3 \qquad \text{etc.}, \tag{35.19}$$

then clearly constitute a set of four anticommuting operators; the commutation of the first three is not affected by the common operator factor ρ_1; $\gamma_4 = \rho_3$ anticommutes with the first three just because of this factor.

Utilizing (35.18), we may now form the four sets of operators (35.16), thus obtaining the following representation of

$$\begin{matrix} \rho_1\boldsymbol{\sigma} & \rho_3 \\ \rho_2\boldsymbol{\sigma} & \rho_1, \\ \rho_3\boldsymbol{\sigma} & \rho_2 \\ -i\boldsymbol{\sigma} & 1 \end{matrix} \tag{35.20}$$

where, for brevity, the three σ-operators have been written as a three-dimensional vector $\boldsymbol{\sigma}$.

It is clear that in this case we do not gain much advantage by utilizing general systems of hypercomplex numbers. These are all collected and displayed in the above simple form, and each of the first three systems is just as suitable as any other for our purposes. Hence we may choose one of them, for example, the first, as the representation of our α-operators, and put

$$\alpha_1 = \rho_1\sigma_1, \qquad \alpha_2 = \rho_1\sigma_2, \qquad \alpha_3 = \rho_1\sigma_3, \qquad \alpha_4 = \rho_3. \tag{35.21}$$

The Matrix Representation of the α-Operators

Each of the σ- and ρ-operators have the eigenvalues ± 1. We may then choose, say, σ_3 and ρ_3 as diagonal matrices with these eigenvalues as diagonal elements; however, the two eigenvalues for each of these quantities furnish four possibilities of combination, so that we must consider the eigenvalues ± 1 twice for each of them, that is introduce four-dimensional matrices. One easily verifies that (35.19) is satisfied by the matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \qquad \sigma_2 = \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix}, \tag{35.22}$$

$$\sigma_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}.$$

Corresponding ρ-matrices may be obtained by interchanging, say, the

second and third rows and columns of these σ-matrices:

$$\rho_1 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \qquad \rho_2 = \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix},$$

$$\rho_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}. \tag{35.23}$$

The matrix representation of the α-operators then follows from (35.22) and (35.23) by ordinary matrix multiplication,

$$\alpha_1 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \qquad \alpha_2 = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix},$$

$$\alpha_3 = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}, \qquad \alpha_4 = \rho_3, \tag{35.24}$$

or in a more compact notation,

$$\alpha_1 = \begin{pmatrix} 0 & \sigma_1 \\ \sigma_1 & 0 \end{pmatrix}, \quad \alpha_2 = \begin{pmatrix} 0 & \sigma_2 \\ \sigma_2 & 0 \end{pmatrix}, \quad \alpha_3 = \begin{pmatrix} 0 & \sigma_3 \\ \sigma_3 & 0 \end{pmatrix}, \quad \alpha_4 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{35.25}$$

Solution of the Force-Free Equation

Using the expression (35.11) for the Hamiltonian, we may now write the wave equation for a free particle in the form

$$(\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z)\psi = \left(\frac{E}{c} - \alpha_4 m_0 c\right)\psi,$$

$$p_x = \frac{h}{2\pi i}\frac{\partial}{\partial x}, \qquad \text{etc.} \tag{35.26}$$

The wave function ψ is here to be regarded as having four components, to be denoted by ψ_1, ψ_2, ψ_3, ψ_4, given in the order corresponding to the eigenvalues of σ_3 and ρ_3 in (35.22) and (35.23). The wave equation (35.26) must therefore be thought of as a set of four simultaneous first-order differential equations.

The individual equations will not be written down here. Since p_x, p_y, and p_z are evidently constants of the motion, all the four components of the wave function will be expressible by the same spatial function

$$\Psi = \exp\left[\frac{2\pi i}{h}(p_x x + p_y y + p_z z)\right], \tag{35.27}$$

where p_x, p_y, p_z are the quantized values of the momenta. Hence the wave function may be written

$$\psi = \{c_1, c_2, c_3, c_4\}\Psi, \tag{35.28}$$

where the four components are now characterized by the purely numerical factors c, that is, $\psi_1 = c_1\Psi$, and so on. For these constants we obtain the linear equations

$$\begin{aligned}
(p_x - ip_y)c_4 + p_z c_3 &= \left(\frac{E}{c} - m_0 c\right)c_1, \\
(p_x + ip_y)c_3 - p_z c_4 &= \left(\frac{E}{c} - m_0 c\right)c_2, \\
(p_x - ip_y)c_2 + p_z c_1 &= \left(\frac{E}{c} + m_0 c\right)c_3, \\
(p_x + ip_y)c_1 - p_z c_2 &= \left(\frac{E}{c} + m_0 c\right)c_4.
\end{aligned} \tag{35.29}$$

Here we can eliminate c_4 and c_3 from the first equation by means of the last two equations, thus obtaining

$$(p_x^2 + p_y^2 + p_z^2)c_1^2 = \left(\frac{E}{c} + m_0 c\right)\left(\frac{E}{c} - m_0 c\right)c_1^2, \tag{35.30}$$

or assuming that $c_1 \neq 0$,

$$\frac{E}{c} = \pm(m_0^2 c^2 + p^2)^{1/2}. \tag{35.31}$$

These two eigenvalues might have been determined directly from the quadratic equation

$$\left(\frac{H}{c}\right)^2 \psi = (p_x^2 + p_y^2 + p_z^2 + m_0^2 c^2)\psi = \left(\frac{E}{c}\right)^2 \psi. \tag{35.32}$$

The substitution of the two eigenvalues (35.31) in the system of equations (35.29) yields two solutions of the latter. The system is evidently underdetermined, and arbitrary values may be chosen for, say, c_1 and c_2. However, we are not primarily interested in the explicit solutions and shall therefore content ourselves with stating that c_3 and c_4 are small relative to one of the constants c_1 and c_2 if the positive energy value is chosen; on the other hand, c_1 and c_2 are small if the negative value is chosen.

This is often expressed by referring to ψ_1 and ψ_2 as the *large*, and ψ_3 and ψ_4 as the *small*, components of the wave function; this applies to the "normal" solutions of the wave equations, that is, to positive energy values. In addition to these, solutions with negative energy appear; here the components ψ_3 and ψ_4 dominate, while ψ_1 and ψ_2 are small of a "relativistic" order of magnitude. As is well known, Dirac's theory relates these latter solutions to the existence of positive electrons.

Considering the limiting case $\mathbf{p} \to 0$, electrons at rest, the components ψ_3 and ψ_4 vanish for the eigenvalue $E = m_0c^2$; correspondingly the components ψ_1 and ψ_2 vanish for $E = -m_0c^2$. We shall not discuss the theory of positive electrons in any more detail but only note that a quantum transition between these two states releases the energy $2m_0c^2$, or around one million electron volts. The theoretical interpretation of this is that a positive and a negative electron coalesce and annihilate each other. Conversely a pair of electrons may by created by a batch of radiation with the energy 1 MeV if the physical conditions are suitable: say, when a photon passes close to an atomic nucleus.

The Wave Equation for an Electron in a Force Field

Dirac's relativistic formulation of the wave equation has turned out to be the correct one for the electron. On the other hand, it need not be valid for other (charged or uncharged) atomic particles. On the contrary, experimental measurements of the spin and magnetic moment of, say, the proton indicate that the equation certainly does not apply for this particle. The equation presently to be stated is thus assumed to hold for the electron only.

We assume that the electron is in a given field of force, that surrounding an atom, for instance, and denote the potential energy of the electron by V. For the electron in a hydrogen atom, or in the field of an atomic nucleus of charge Ze, we shall then have

$$V = -\frac{Ze^2}{r} \quad \text{or} \quad V = -e\Phi, \quad \Phi = \frac{Ze}{r}. \tag{35.33}$$

The potential energy V is here of an electromagnetic nature and is expressible by means of the electric potential Φ. We shall assume that V may also

contain contributions from other (nonelectromagnetic) interactions, and hence use the general notation V in our formulation of the wave equation.

By the preceding considerations, and particularly by (35.11), we may now assume that the relativistic wave equation is expressible in the form

$$H\psi = E\psi, \tag{35.34}$$

where

$$H = c\left[\alpha_1\left(p_x + \frac{e}{c}A_x\right) + \alpha_2\left(p_y + \frac{e}{c}A_y\right) + \alpha_3\left(p_z + \frac{e}{c}A_z\right) + \alpha_4 m_0 c\right] + V. \tag{35.35}$$

36. THE SPIN AND MAGNETIC MOMENT OF THE ELECTRON

Constants of Motion in a Central Field

To begin with, we assume that no electromagnetic field is present, apart from an electrostatic field that is included in the potential energy V; the latter is assumed to have the form $V = V(r)$ corresponding to a central field, so that it commutes with the orbital spin $\mathbf{m} = \mathbf{r} \times \mathbf{p}$.

Thus we write

$$H = c\{\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z + \alpha_4 m_0 c\} + V(r), \tag{36.1}$$

and it is now easily seen that the components of orbital spin are no longer constants of the motion. Let us consider, in particular,

$$m_z = xp_y - yp_x. \tag{36.2}$$

Due to the coordinates x and y appearing in this expression, m_z does not commute with p_x and p_y in H; using the commutation rules for coordinates and momenta, we find that

$$Hm_z - m_z H = \frac{hc}{2\pi i}(\alpha_1 p_y - \alpha_2 p_x). \tag{36.3}$$

If it were possible to find another quantity, the commutator of which with H had the same form as (36.3), we might construct a compound quantity that did commute with H. It is, of course, impossible to construct such a quantity as a function of coordinates and momenta alone. However, we may utilize the α-operators to define an operator quantity that commutes with all terms in H, except the first two; this is the product operator $\alpha_1\alpha_2$. The commutator of the latter with H is by (35.12) and (35.13) found to be

$$H\alpha_1\alpha_2 - \alpha_1\alpha_2 H = 2c\{\alpha_2 p_x - \alpha_1 p_y\}. \tag{36.4}$$

Hence it follows that

$$M_z = m_z + s_z \tag{36.5}$$

is commutative with H, and thus a possible constant of the motion, if we write

$$s_z = \frac{1}{2}\frac{h}{2\pi i}\alpha_1\alpha_2 = \frac{1}{2}\frac{h}{2\pi}\sigma_3, \tag{36.6}$$

where σ_3 is defined by the four-dimensional matrices (35.21) and (35.22).

Similar results are obtained for the remaining components of the vector

$$\mathbf{M} = \mathbf{m} + \mathbf{s}, \qquad \mathbf{s} = \frac{1}{2}\frac{h}{2\pi}\boldsymbol{\sigma}. \tag{36.7}$$

We may therefore regard $\mathbf{M}$ as the total angular momentum of the electron, composed of the orbital spin $\mathbf{m}$ and the intrinsic spin $\mathbf{s}$. Hence we see that the mechanical spin of the electron appears as a direct consequence of Dirac's relativistic wave equation, that is, as a particular relativistic effect.

Just as for the orbital spin only, we find that the components of $\mathbf{M}$ are not mutually commutative; on the other hand, $\mathbf{M}^2$ commutes with each of these components. The quantities that may be quantized for an electron in a central field are thus M_z and $\mathbf{M}^2$; the eigenfunctions for these operators will be deduced later.

The Magnetic Moment of the Spinning Electron

We now consider the wave equation for an electron in a general electromagnetic field, replacing H by the operator

$$E = -\frac{h}{2\pi i}\frac{\partial}{\partial t}. \tag{36.8}$$

This equation may then be written

$$(E + e\Phi)\psi = \{\boldsymbol{\alpha}(c\mathbf{p} + e\mathbf{A}) + \alpha_4 m_0 c^2\}\psi, \tag{36.9}$$

where $\boldsymbol{\alpha}$ is the three-dimensional vector operator $(\alpha_1, \alpha_2, \alpha_3)$. We multiply this equation by $E + e\Phi$, commute the operators on the right-hand side, and substitute the expression (36.9) for $(E + e\Phi)\psi$ on this side; after some ordering of the equation we then obtain

$$\begin{aligned}\{(E + e\Phi)^2 - m_0^2c^4\}\psi = (c\mathbf{p} + e\mathbf{A})^2\psi \\ + ec\frac{h}{2\pi i}\left\{\alpha_2\alpha_3\left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}\right) + \cdots\right. \\ \left. + \alpha_1\left(-\frac{1}{c}\frac{\partial A_x}{dt} - \frac{\partial \Phi}{\partial x}\right) + \cdots\right\}\psi.\end{aligned} \tag{36.10}$$

Division by $2m_0c^2$ then leads to

$$\frac{E + e\Phi + m_0c^2}{2m_0c^2}\{E - m_0c^2 + e\Phi\}\psi = \frac{1}{2m_0}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2\psi + \frac{e}{2m_0c}\frac{h}{2\pi}\left\{\boldsymbol{\sigma}\mathbf{H} + \frac{1}{i}\boldsymbol{\alpha}\mathbf{E}\right\}, \quad (36.11)$$

since $\alpha_2\alpha_3 = i\sigma_1$, and so forth. The first factor on the left-hand side has the value unity in nonrelativistic physics and $E - m_0c^2$ is the nonrelativistic total energy. The additional energy corresponding to the last two terms in (36.11) may thus be interpreted to indicate that the electron itself possesses a magnetic moment and an electric dipole moment.

The magnetic moment may, by (36.7) and (36.11), be written

$$\boldsymbol{\mu}_s = \frac{e}{m_0c}\mathbf{s}. \quad (36.12)$$

Thus the ratio between the magnetic moment $\boldsymbol{\mu}_s$ and the mechanical spin $\mathbf{s}$ of the electron is twice as large as the corresponding ratio $e/2m_0c$ for the orbital spin. This factor 2 originally represented a rather ad hoc assumption in the hypothesis of an intrinsic electron spin; it is now seen to be directly deducible from the relativistic wave equation of Dirac.

The Relativistic Spin Correction

The most important part of the relativistic effect on the atomic energy levels is that expressed by the first additional factor on the left-hand side of (36.11). Disregarding the magnetic and electric moments, the simplified one-component equation will give a fine-structure formula, where the correct values $k = l + 1$ and $k = l$ for the earlier "biquantum number" has been replaced by the common value $k = l + \frac{1}{2}$. The number $l = 0, 1, \cdots$ is the wave-mechanical azimuthal quantum number.

In (36.11) it is only the term $\boldsymbol{\alpha}\mathbf{E}$ that connects the "large" and "small" components ψ_1, ψ_2 and ψ_3, ψ_4 of the four-component wave function corresponding to (respectively) positive and negative energy states, that is, to the rest energies m_0c^2 and $-m_0c^2$. This term will thus give rise to a purely relativistic effect, which is that referred to earlier as a parallel or antiparallel adjustment of the intrinsic electron spin, relative to its orbital spin.

From the relativistic consideration of electromagnetic fields we know that a field which is purely electric in one coordinate system may also have magnetic components in another system, and vice versa. Similarly we must expect that a purely magnetic moment may appear partly as an electric dipole moment; thus it is natural that the spinning electron exhibits such an

electric moment which may be written

$$\mathbf{p}_s = \frac{e}{2m_0c}\frac{h}{2\pi i}\boldsymbol{\alpha} \tag{36.13}$$

by (36.11).

This interpretation is somewhat abstract, even more so as the electric dipole moment appears in an imaginary form. We shall therefore use the equation

$$2i\alpha_1 = 2i\rho_1\sigma_1 = \rho_1(\sigma_2\sigma_3 - \sigma_3\sigma_2) = \sigma_2\alpha_3 - \alpha_3\sigma_2 \tag{36.14}$$

or

$$2i\boldsymbol{\alpha} = \boldsymbol{\sigma} \times \boldsymbol{\alpha} \tag{36.14a}$$

to express the last additional term in (36.11) as

$$-\frac{e}{2m_0c}(\mathbf{s} \times \boldsymbol{\alpha})\mathbf{E} = -\frac{e\mathbf{s}}{2m_0c}(\boldsymbol{\alpha} \times \mathbf{E}). \tag{36.15}$$

Here we shall allow ourselves to interpret α in the way indicated by (35.7), as

$$\boldsymbol{\alpha} = \frac{\mathbf{v}}{c} = \frac{\mathbf{p}}{mc} \approx \frac{\mathbf{p}}{m_0c}. \tag{36.16}$$

If, furthermore, E is due to a central field, that is,

$$\mathbf{E} = -\frac{1}{r}\frac{d\Phi}{dr}\cdot\mathbf{r}, \tag{36.17}$$

the additional energy becomes approximately,

$$-\frac{e\mathbf{s}}{2m_0c}(\boldsymbol{\alpha} \times \mathbf{E}) \approx \frac{e}{2m_0^2c^2}\left(-\frac{1}{r}\frac{d\Phi}{dr}\right)\mathbf{sm}. \tag{36.18}$$

If, in particular, $\Phi(r)$ is the Coulomb field from a nucleus with the charge Ze, the additional energy becomes

$$\Delta E \approx \frac{e}{m_0c}\cdot\frac{Ze}{m_0c}\cdot\frac{1}{r^3}\mathbf{sm}. \tag{36.19}$$

Here $\mathbf{m} = \mathbf{r} \times \mathbf{p}$ is the orbital spin, as usual, and this last relativistic term thus furnishes the coupling between the orbital and intrinsic spins for the electron. As shown previously it gives rise to a doubling of the energy levels, and corrects the latter in a very close correspondence with the exact relativistic fine-structure formula.

The above reformulation and simplification of the wave equation, where approximations have only been introduced in (36.18) and (36.19), allows us to ignore the "small" components ψ_3 and ψ_4 of the relativistic wave function.

Thus we may establish a new approximate wave equation, retaining the last two spin terms of (36.11) but expressing the latter only in terms of the spin matrices $\boldsymbol{\sigma}$; the latter may then be used in their earlier two-dimensional form, corresponding to the remaining "large" components ψ_1 and ψ_2 of the wave function.

This form has the advantage of being more easily adaptable to problems involving several electrons. Concerning the one-electron problem, we have now discussed several times the effect of the electron spin in some detail; and we shall therefore not consider this "semirelativistic" wave equation any more.

37. THE RELATIVISTIC WAVE EQUATION FOR THE HYDROGEN ATOM

Spin Eigenvalues and Eigenfunctions

As shown earlier it is the operator

$$\mathbf{M} = \mathbf{m} + \frac{1}{2}\frac{h}{2\pi}\boldsymbol{\sigma} \tag{37.1}$$

that commutes with H and consequently may be quantized; hence we must take $\mathbf{M}$ to represent the total angular momentum.

We now consider the operator

$$M_z = m_z + \frac{1}{2}\frac{h}{2\pi}\sigma_3. \tag{37.2}$$

Here σ_3 has the eigenvalues ± 1, so that the z-component of the intrinsic electron spin has the two possible values

$$s_z = \pm\frac{1}{2}\frac{h}{2\pi}. \tag{37.3}$$

This corresponds to a wave function with two components which are those referred to previously as ψ_1 and ψ_2.

Let us now consider a particular eigenvalue

$$M_z' = \frac{h}{2\pi}m_j \tag{37.4}$$

of M_z. Utilizing the earlier two-dimensional matrix representation

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{37.5}$$

we obtain the two eigenvalue equations

$$\left(\frac{1}{i}\frac{\partial}{\partial\varphi}+\frac{1}{2}\right)\psi_1 = m_j\psi_1,$$
$$\left(\frac{1}{i}\frac{\partial}{\partial\varphi}-\frac{1}{2}\right)\psi_2 = m_j\psi_2 \tag{37.6}$$

with the solutions

$$\psi_1 = c_1 \exp\,[i(m_j - \tfrac{1}{2})\varphi], \qquad \psi_2 = c_2 \exp\,[i(m_j + \tfrac{1}{2})\varphi]. \tag{37.7}$$

Here c_1 and c_2 are constants with respect to variation of the angle φ; however, they may be taken to depend on the polar angle ϑ and the radius vector r.

It follows from (37.6) that m_j must be half-integral in order that the wave function be uniquely determined; hence we may conclude that the spin squared has the eigenvalues

$$\mathbf{M}^2 = j(j+1)\left(\frac{h}{2\pi}\right)^2, \tag{37.8}$$

where j also is half-integral. For m_j we must then have

$$m_j = -j, -j+1, \cdots, -\tfrac{1}{2}, \tfrac{1}{2}, \cdots, j-1, j. \tag{37.9}$$

Consider now the equation

$$\mathbf{M}^2 = \left(\mathbf{m} + \frac{1}{2}\frac{h}{2\pi}\boldsymbol{\sigma}\right)^2 = \mathbf{m}^2 + \mathbf{m}\boldsymbol{\sigma}\frac{h}{2\pi} + \frac{3}{4}\left(\frac{h}{2\pi}\right)^2. \tag{37.10}$$

It shows that $\mathbf{m}^2$ and $\mathbf{m}\boldsymbol{\sigma}$ may be quantized simultaneously with $\mathbf{M}^2$ despite the fact that they do not commute with the energy. The only possible values for $\mathbf{m}^2$ are then

$$\mathbf{m}^2 = l(l+1)\left(\frac{h}{2\pi}\right)^2 \qquad l = j \mp \tfrac{1}{2}, \tag{37.11}$$

corresponding to, respectively, parallel and antiparallel addition of orbital and intrinsic electron spins. Hence we find the corresponding values of $\mathbf{m}\boldsymbol{\sigma}$ to be

$$\mathbf{m}\boldsymbol{\sigma} + \frac{h}{2\pi} = \pm\left(j+\frac{1}{2}\right)\frac{h}{2\pi}. \tag{37.12}$$

Using the σ-matrices (37.5), we easily obtain the simultaneous equations

$$(m_x - im_y)\psi_2 + \left(m_z + \frac{h}{2\pi}\right)\psi_1 = \pm\left(j+\frac{1}{2}\right)\frac{h}{2\pi}\psi_1,$$
$$(m_x + im_y)\psi_1 + \left(-m_z + \frac{h}{2\pi}\right)\psi_2 = \pm\left(j+\frac{1}{2}\right)\frac{h}{2\pi}\psi_2. \tag{37.13}$$

With the known eigenvalues for m_z, which may be found from (37.7), this yields

$$\begin{aligned}(m_x - im_y)\psi_2 &= (j - m_j)\psi_1,\\ (m_x + im_y)\psi_1 &= (j + m_j)\psi_2,\end{aligned} \qquad l = j - \tfrac{1}{2}, \tag{37.14}$$

and

$$\begin{aligned}(m_x - im_y)\bar{\psi}_2 &= -(j + 1 + m_j)\bar{\psi}_1,\\ (m_x + im_y)\bar{\psi}_1 &= -(j + 1 - m_j)\bar{\psi}_2.\end{aligned} \qquad l = j + \tfrac{1}{2}. \tag{37.15}$$

Here

$$\begin{aligned}(m_x - im_y) &= e^{-i\varphi}\left(-\frac{\partial}{\partial\vartheta} - \frac{\cos\vartheta}{\sin\vartheta}\frac{1}{i}\frac{\partial}{\partial\varphi}\right),\\ (m_x + im_y) &= e^{i\varphi}\left(\frac{\partial}{\partial\vartheta} - \frac{\cos\vartheta}{\sin\vartheta}\frac{1}{i}\frac{\partial}{\partial\varphi}\right)\end{aligned} \tag{37.16}$$

are the previously discussed operators for the orbital spin.

By means of the last equations (37.14) and (37.15) we find immediately that

$$\Phi_1 = (j + m_j)Y_{j-\frac{1}{2}}^{m_j-\frac{1}{2}}, \qquad \Phi_2 = -Y_{j-\frac{1}{2}}^{m_j+\frac{1}{2}}, \qquad l = j - \tfrac{1}{2} \tag{37.17}$$

and

$$\bar{\Phi}_1 = (j + 1 - m_j)Y_{j+\frac{1}{2}}^{m_j-\frac{1}{2}}, \qquad \bar{\Phi}_2 = Y_{j+\frac{1}{2}}^{m_j-\frac{1}{2}}, \qquad l = j + \tfrac{1}{2}, \tag{37.18}$$

where we have denoted the angle-dependent part of the wave function ψ by Φ and written $\Phi_l^m = P_{\cdot}^{m}(\cos\vartheta)e^{im\psi}$. The first equations (37.14) and (37.15) will then automatically be satisfied, since they correspond to the differential equations for the spherical functions. We must, however, note that the expressions (37.17) and (37.18) only hold for positive values of m_j. We shall not require the corresponding explicit expressions for negative m_j, and consequently omit these here.

Simultaneous Spin Eigenfunctions

Since the spin operator (37.12) does not commute with the energy function for a central field, it may not be quantized; hence the orbital spin may not be thought of as uniquely determined. As a consequence of this we must consider both functions Φ and $\bar{\Phi}$ in (37.17) and (37.18), the one set for the large components ψ_1, ψ_2 and the other for the small components ψ_3, ψ_4.

This is most easily done by introducing a new operator k, defined by

$$k\frac{h}{2\pi} = \left(\mathbf{m\sigma} + \frac{h}{2\pi}\right)\alpha_4. \tag{37.19}$$

By (37.10) $\mathbf{m\sigma}$ commutes with $\mathbf{M}$, and since α_4 also commutes with the components of $\mathbf{M}$, then k and $\mathbf{M}$ are commutative. We shall show later that k

also commutes with the energy function. Hence it may be quantized, and we now show that its eigenvalues for a given j are

$$k = \pm(j + \tfrac{1}{2}). \tag{37.20}$$

Using the commutation rules for orbital and intrinsic spins, we easily find that

$$\left(k\frac{h}{2\pi}\right)^2 = \mathbf{m}^2 + 2\mathbf{m}\boldsymbol{\sigma}\frac{h}{2\pi} + \left(\frac{h}{2\pi}\right)^2 + (m_x m_y - m_y m_x)\sigma_x\sigma_y + \cdots$$
$$= \mathbf{m}^2 + \mathbf{m}\boldsymbol{\sigma}\frac{h}{2\pi} + \left(\frac{h}{2\pi}\right)^2 = \mathbf{M}^2 + \frac{1}{4}\left(\frac{h}{2\pi}\right)^2 = \left(j + \frac{1}{2}\right)^2\left(\frac{h}{2\pi}\right)^2. \tag{37.21}$$

Thus the correct form of (37.12) is

$$\mathbf{m}\boldsymbol{\sigma} + \frac{h}{2\pi} = k\alpha_4\frac{h}{2\pi} = \pm\left(j + \frac{1}{2}\right)\alpha_4\frac{h}{2\pi}. \tag{37.22}$$

Evidently the change of sign in k is canceled by the negative sign of the last two diagonal elements of α_4, so that the spin function for positive k is Φ_1, Φ_2 for the large components, and $\bar{\Phi}_1$, $\bar{\Phi}_2$ for the small ones; for negative k, it is vice versa.

We now reformulate the relativistic equation for the Kepler problem

$$\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z + \alpha_4 m_0 c = \frac{E}{c} + \frac{Ze^2}{cr} \tag{37.23}$$

to read

$$p_x^2 + p_y^2 + p_z^2 + m_0^2 c^2 = \left(\frac{E}{c} + \frac{Ze^2}{cr}\right)^2 + \frac{Ze^2}{cr^2}\frac{h}{2\pi i}\varepsilon \tag{37.24}$$

and

$$\varepsilon = \alpha_1\frac{x}{r} + \alpha_2\frac{y}{r} + \alpha_3\frac{z}{r}, \qquad \varepsilon^2 = 1. \tag{37.25}$$

It is now easily shown that k and ε commute

$$[\varepsilon, k] = \left[\varepsilon, \frac{2\pi}{h}\mathbf{m}\boldsymbol{\sigma}\alpha_4\right] + 2\varepsilon\alpha_4 = 0. \tag{37.26}$$

We have

$$\left[\varepsilon, \frac{2\pi}{ih} m_z\alpha_1\alpha_2\alpha_4\right] = -\left(\alpha_1\frac{x}{r} + \alpha_2\frac{y}{r}\right)\alpha_4 = \frac{4\pi}{ih} m_z\frac{z}{r}\alpha_1\alpha_2\alpha_3\alpha_4. \tag{37.27}$$

Thus by the addition of (37.27) and two similar equations we obtain (37.26), since $\mathbf{mr} = 0$. In a completely analogous way, we may show that $[\boldsymbol{\alpha}\mathbf{p}, k] = 0$,

so that k commutes with the energy function in (37.23). Strictly speaking, however, this is not necessary, since it all follows from (37.24) to (37.26). Moreover we have complete symmetry, with respect to k, between $\boldsymbol{\alpha}\mathbf{p}$ and $\boldsymbol{\alpha}\mathbf{r}$ in the operator ε.

This operator may be expressed by the four-dimensional matrix

$$\varepsilon = \begin{pmatrix} 0 & 0 & \cos\vartheta & \sin\vartheta\, e^{-i\varphi} \\ 0 & 0 & \sin\vartheta e^{i\varphi} & \cos\vartheta \\ \cos\vartheta & \sin\vartheta e^{-i\varphi} & 0 & 0 \\ \sin\vartheta e^{i\varphi} & \cos\vartheta & 0 & 0 \end{pmatrix}. \tag{37.28}$$

With the particular normalization chosen for the functions (37.17) and (37.18) it may now be shown that

$$\varepsilon\{R_1\Phi_1,\ R_1\Phi_2,\ R_2\bar{\Phi}_1,\ R_2\bar{\Phi}_2\} = \{R_2\Phi_1,\ R_2\Phi_2,\ R_1\bar{\Phi}_1,\ R_1\bar{\Phi}_2\}. \tag{37.29}$$

This corresponds to the equation

$$\Phi_1 = \bar{\Phi}_1 \cos\vartheta + \Phi_2 \sin\vartheta e^{-i\varphi} \tag{37.30}$$

and three corresponding equations, which may easily be found by means of the matrix ε. Once we have thus fixed the spin eigenfunctions the radial part of the wave equation may be regarded as a two-component function

$$R = \{R_1,\ R_2\}. \tag{37.31}$$

The operator ε then, by (37.29), only causes a permutation of these components. Thus letting the expression (37.31) correspond to $k = j + \frac{1}{2}$, we may write

$$\bar{R} = \{\bar{R}_1,\ \bar{R}_2\}. \tag{37.32}$$

say, for $k = -(j + \frac{1}{2})$. The corresponding complete expressions for the wave function are then

$$\begin{aligned} \{\psi_1, \psi_2, \psi_3, \psi_4\} &= \{R_1[\Phi_1, \Phi_2],\ R_2[\bar{\Phi}_1, \bar{\Phi}_2]\}, \\ \{\psi_1, \psi_2, \psi_3, \psi_4\} &= \{\bar{R}_1[\bar{\Phi}_1, \bar{\Phi}_2],\ \bar{R}_2[\Phi_1, \Phi_2]\}. \end{aligned} \tag{37.33}$$

Since the operators ε and α_4 anticommute, we may represent them by two-dimensional matrices, say,

$$\varepsilon = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad i\varepsilon\alpha_4 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \alpha_4 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{37.34}$$

with regard to R and $\bar{R}$ in (37.31) and (37.32).

38. THE COMPLETE SOLUTION OF THE RADIAL WAVE EQUATIONS

The Relativistic Fine-Structure Formula

For the determination of the energy levels, that is, of the relativistic fine-structure formula, we may use (37.24), writing

$$p_x^2 + p_y^2 + p_z^2 = \frac{1}{r^2} p_r r^2 p_r + \frac{\mathbf{m}^2}{r^2},$$
$$\mathbf{m}^2 = \mathbf{M}^2 + \left(\frac{1}{4} - k\alpha_4\right)\left(\frac{h}{2\pi}\right)^2 = (k^2 - k\alpha_4)\left(\frac{h}{2\pi}\right)^2 \tag{38.1}$$

by (37.10) and (37.22). Hence we see that the operator k reappears indirectly, through $\mathbf{m}$. By means of the abbreviations

$$\lambda = (k^2 - Z^2\alpha^2)^{1/2}, \qquad \alpha = \frac{2\pi e^2}{hc} \approx \frac{1}{137}, \tag{38.2}$$

where α is the well-known fine-structure constant of Sommerfeld, the wave equation (37.24) may be written

$$\left\{\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\lambda(\lambda - \delta)}{r^2} + \left(\frac{2\pi}{h}\right)^2\left(\frac{E^2}{c^2} - m_0^2c^2 + \frac{2E}{c^2}\frac{Ze^2}{r}\right)\right\}\psi = 0. \tag{38.3}$$

Here δ is a new operator,

$$\delta = \frac{1}{\lambda}(k\alpha_4 + iZ\alpha\varepsilon), \qquad \delta^2 = 1, \tag{38.4}$$

with the square value unity. Multiplying (38.3) by, respectively, $1 + \delta$ and $1 - \delta$, we obtain the two independent equations

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\lambda(\lambda \mp 1)}{r^2} + \left(\frac{2\pi}{h}\right)^2\left(\frac{E^2}{c^2} - m_0^2c^2 + \frac{2E}{c^2}\frac{Ze^2}{r}\right)\right](1 \pm \delta)\psi = 0. \tag{38.5}$$

These two equations have the same energy eigenvalues which may easily be found by comparison with the radial wave equation for the hydrogen atom. We need only replace the azimuthal quantum number l by $\lambda - 1$ and λ in the energy equation for this atom, and then introduce the radial quantum numbers n_1 and n_2, writing

$$n^* = \lambda + n_1 = \lambda + 1 + n_2 = n - |k| + \lambda,$$
$$n_1 = n_2 + 1 = n - |k|, \tag{38.6}$$

where n is the true principal quantum number and n^* the corresponding "effective" quantum number.

In our calculations we now formally substitute the nuclear charge $Z' = ZE/m_0c^2$ for Z; and the previously considered energy E is similarly, in accordance with (38.5), replaced by $E' = (E^2 - m_0^2c^4)/2m_0c^2$. In this way we obtain

$$\frac{m_0^2c^4}{E^2} - 1 = \frac{2Z^2Rh}{m_0c^2(n^*)^2} = \frac{Z^2\alpha^2}{(n^*)^2}, \qquad n^* = n - |k| + (k^2 - Z^2\alpha^2)^{1/2} \tag{38.7}$$

which is the relativistic fine-structure formula.

Simultaneous Radial Wave Equations

We have deviated somewhat from Dirac's method of exposition, where two simultaneous first-order differential equations for R_1 and R_2 in (37.31) and (37.32) are deduced. Our method, which employs the second-order equation (38.3), is more familiar; however, we must have recourse to at least one of the first-order equations mentioned above in order to find the ratio between the magnitudes of R_1 and R_2. Hence we shall now deduce these two equations.

We consider (37.23) and multiply it by ε. Writing

$$xp_x + yp_y + zp_z = \frac{h}{2\pi i} r \frac{\partial}{\partial r} = rp_r, \tag{38.8}$$

we obtain

$$\left(p_r + \frac{i\boldsymbol{\sigma}\mathbf{m} - (Ze^2/c)\varepsilon}{r}\right)\psi = \left(\frac{E}{c}\varepsilon + m_0c\alpha_4\varepsilon\right)\psi, \tag{38.9}$$

since $\varepsilon\alpha_4 = -\alpha_4\varepsilon$. By means of (37.22) and the equations (38.2) and (38.4) this may be reformulated as

$$\frac{h}{2\pi i}\left(\frac{\partial}{\partial r} + \frac{1 - \lambda\delta}{r}\right)\psi = \left(\frac{E}{c}\varepsilon + m_0c\alpha_4\varepsilon\right)\psi. \tag{38.10}$$

We now eliminate ε in the first term on the right-hand side, using the identity

$$\varepsilon = \delta^2\varepsilon = \delta(\delta\varepsilon) = \frac{\delta}{\lambda}(k\alpha_4\varepsilon + iZ\alpha), \tag{38.11}$$

and thus find

$$\frac{h}{2\pi i}\left(\frac{\partial}{\partial r} + \frac{1 - \lambda\delta}{r} + \frac{2\pi}{h}\frac{E}{c}\frac{Z\alpha}{\lambda}\delta\right)\psi = \left(\frac{E}{e}\frac{k}{\lambda}\delta + m_0c\right)\alpha_4\varepsilon\psi. \tag{38.12}$$

Multiplying this equation by, respectively, $(1 + \delta)$ and $\alpha_4\varepsilon(1 - \delta)$, and

putting

$$(1+\delta)\psi = v_1, \qquad (1-\delta)\psi = v_2, \qquad \psi = \tfrac{1}{2}(v_1 + v_2), \tag{38.13}$$

we then finally obtain

$$\begin{aligned} \frac{h}{2\pi i}\left(\frac{\partial}{\partial r} + \frac{1-\lambda}{r} + \frac{2\pi}{h}\frac{E}{c}\frac{Z\alpha}{\lambda}\right)v_1 &= \left(\frac{E}{c}\frac{k}{\lambda} + m_0 c\right)\alpha_4 \varepsilon v_2, \\ \frac{h}{2\pi i}\left(\frac{\partial}{\partial r} + \frac{1+\lambda}{r} - \frac{2\pi}{h}\frac{E}{c}\frac{Z\alpha}{\lambda}\right)\alpha_4 \varepsilon v_2 &= \left(\frac{E}{c}\frac{k}{\lambda} - m_0 c\right)v_1. \end{aligned} \tag{38.14}$$

We must here note that v_1 and v_2 satisfy the equations

$$\delta v_1 = v_1, \qquad \delta v_2 = -v_2. \tag{38.15}$$

This means that the four components of these wave equations have different numerical magnitudes, even though their analytical dependence on r is the same. It is possible to simplify the matter by writing

$$v_1 = c_1(1+\delta)u_1, \qquad v_2 = c_2\alpha_4\varepsilon(1+\delta)u_2, \tag{38.16}$$

since we may then assume that the four components of u_1 and u_2 are equal. Multiplication of u_1 and u_2 by $(1+\delta)$ changes the mutual ratios between the coefficients in the same way; hence we obtain the same simultaneous differential equations for u_1 and u_2 as for $(1+\delta)u_1$ and $(1+\delta)u_2$, namely,

$$\begin{aligned} \frac{h}{2\pi i}\left(\frac{\partial}{\partial r} + \frac{1-\lambda}{r} + \frac{2\pi}{h}\frac{E}{c}\frac{Z\alpha}{\lambda}\right)c_1 u_1 &= -\left(m_0 c + \frac{E}{c}\frac{k}{\lambda}\right)c_2 u_2, \\ \frac{h}{2\pi i}\left(\frac{\partial}{\partial r} + \frac{1+\lambda}{r} - \frac{2\pi}{h}\frac{E}{c}\frac{Z\alpha}{\lambda}\right)c_2 u_2 &= \left(m_0 c - \frac{E}{c}\frac{k}{\lambda}\right)c_1 u_1. \end{aligned} \tag{38.17}$$

Eliminating one of the functions, we obtain the differential equations (38.5) with the upper and lower signs corresponding to v_1 and v_2, respectively. Hence we may put

$$\begin{aligned} &u_1 = \text{const}\, e^{-\xi/2}\xi^{\lambda-1}L_{n^*+\lambda-1}^{2\lambda-1}(\xi), \quad u_2 = \text{const}\, e^{-\xi/2}\xi^{\lambda}L_{n^*+\lambda}^{2\lambda+1}(\xi), \\ &\xi = \frac{E}{m_0 c^2}\cdot\frac{2Z}{a_H}\cdot\frac{r}{n^*}, \quad n^* = n - |k| + \lambda, \quad \lambda = (k^2 - Z^2\alpha^2)^{1/2}. \end{aligned} \tag{38.18}$$

The constants in these expressions are assumed to be chosen such that

$$\int_0^\infty u_1^2 r^2\, dr = 1, \qquad \int_0^\infty u_2^2 r^2\, dr = 1. \tag{38.19}$$

Determination of the Radial Wave Functions

Multiplying the equations (38.17) by $u_2 r^2$ and $u_1 r^2$, respectively, and integrating, we may determine the ratio between c_1 and c_2; we find

$$\frac{c_2^2}{c_1^2} = \frac{m_0 c^2/E - k/\lambda}{m_0 c^2/E + k/\lambda}. \tag{38.20}$$

Changing the sign of k yields the reciprocal ration. Moreover (38.20) is negative, so that c_2/c_1 is imaginary. In order to determine this ratio uniquely we must fix the signs of the power terms appearing in the Laguerre polynomials (38.18). Let us assume that the highest power term in each of them has the same sign; the correspondingly lowest terms will then have opposite signs. From the last equation it then evidently follows that c_2/c_1 is positive imaginary for positive k, and c_1/c_2 positive imaginary for negative k. Using the fine-structure formula and the relation $k^2 = \lambda^2 + Z^2\alpha^2$, we may deduce that

$$\begin{aligned} \frac{c_2}{c_1} &= \mu i \frac{Z\alpha}{2\lambda}, \qquad k > 0, \\ \frac{c_1}{c_2} &= \mu i \frac{Z\alpha}{2\lambda}, \qquad k < 0, \\ \mu &= 2(1 - \lambda^2/n^{*2})^{1/2}/(m_0c/E + |k|\lambda) \approx (1 - \lambda^2/n^{*2})^{1/2}. \end{aligned} \tag{38.21}$$

By means of (38.13), (38.16), and (38.19) we may now construct the radial eigenfunctions R_1, R_2, and R_3 in (37.33). For $k > 0$ we put $c_1 = 1_0$ and for $k < 0$, $c_2 = 1$. First we write the two-dimensional form of the matrices

$$\begin{aligned} \frac{1+\delta}{2} &= \frac{1}{2\lambda}\begin{pmatrix} \lambda + k & iZ\alpha \\ iZa & \lambda - k \end{pmatrix}, \\ \alpha_4\varepsilon\frac{1+\delta}{2} &= \frac{1}{2\lambda}\begin{pmatrix} iZ\alpha & \lambda - k \\ -(\lambda + k) & -iZ\alpha \end{pmatrix}. \end{aligned} \tag{38.22}$$

Since these matrices are to be applied to functions, the two components of which are equal in magnitude, they may be replaced by the matrices

$$\frac{1}{2\lambda}\begin{bmatrix} \lambda + k + iZ\alpha & 0 \\ 0 & \lambda - k + iZ\alpha \end{bmatrix}, \quad \frac{1}{2\lambda}\begin{bmatrix} \lambda - k + iZ\alpha & 0 \\ 0 & -(\lambda + k + iZ\alpha \end{bmatrix}. \tag{38.23}$$

Furthermore we may neglect $iZ\alpha$ in comparison with $\lambda + |k|$, and $\lambda - |k|$ in comparison with $iZ\alpha$, as a relativistic approximation; moreover $(\lambda + |k|)/2\lambda$ may be replaced by unity. This yields the approximate matrices

$$\begin{aligned} \frac{1+\delta}{2} &\to \begin{bmatrix} 1 & 0 \\ 0 & iZ\alpha/2\lambda \end{bmatrix}, \quad \alpha_4\varepsilon\frac{1+\delta}{2} \to \begin{bmatrix} iZ\alpha/2\lambda & 0 \\ 0 & -1 \end{bmatrix}, \qquad k > 0, \\ \frac{1+\delta}{2} &\to \begin{bmatrix} iZ\alpha/2\lambda & 0 \\ 0 & 1 \end{bmatrix}, \quad \alpha_4\varepsilon\frac{1+\delta}{2} \to \begin{bmatrix} 0 & \\ 0 & -iZ\alpha/2\lambda \end{bmatrix}, \qquad k < 0. \end{aligned} \tag{38.24}$$

which leads in turn to the following expressions for the radial eigenfunctions

$$\begin{aligned}\{R_1, R_2\} &= \{u_1 - \left(\frac{Z\alpha}{2\lambda}\right)^2 \mu u_2, \quad \left(\frac{iZ\alpha}{2\lambda}\right)(u_1 - \mu u_2)\}, \\ \{\bar{R}_1, \bar{R}_2\} &= \{u_2 - \left(\frac{Z\alpha}{2\lambda}\right)^2 \mu u_1, \quad -\left(\frac{iZ\alpha}{2\lambda}\right)(u_2 - \mu u_1)\}.\end{aligned} \tag{38.25}$$

The quantity $\alpha = 2\pi e^2/hc$ here represents the relativistic effect. If we let it approach zero, we shall also have $R_2, \bar{R}_2 \to 0$; that is, in general, the small components $\psi_3, \psi_4 \to 0$. Actually the last term of the first component of the equations (38.25) may also be neglected in the approximation employed above, since it contains α^2, the square of the fine-structure constant.

CHAPTER 6

General Perturbation Theory

39. PERTURBATION OF DISCRETE STATIONARY STATES

Unperturbed and Perturbed States

In general, atomic and molecular problems may not be solved by elementary methods, such as in the previously given examples of the harmonic oscillator, the fixed and free rotator, and the hydrogen atom and homologous ions. This is, as a rule, due to the fact that the Hamiltonian contains terms of a complicated analytical character, arising from interactions between the particles of the system or from other disturbing influences. It is often possible to isolate such terms and collect them in a separate perturbation term, which we might denote by H', in the energy function; the remainder of this function, which we shall assume represents the principal part of the energy, will then be denoted by H°. For simplicity, we assume that H° is of such a character that we would obtain relatively simple elementary solutions of our problem if it represented the total energy. Thus we write the energy function as

$$H = H^\circ + H', \tag{39.1}$$

or sometimes as

$$H = H^\circ + \varepsilon H' \tag{39.1a}$$

if we desire to express the order of magnitude of the perturbation, relative to the energy of the unperturbed system, by a parameter ε. For the moment we shall use the form (39.1).

As an example of a perturbed Hamiltonian we might consider a two-electron atom:

$$\begin{aligned} H^\circ &= \frac{1}{2m}\left(\frac{h}{2\pi i}\right)^2(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2}, \\ H' &= \frac{e^2}{r_{12}}. \end{aligned} \tag{39.2}$$

Here H' represents the interaction, that is, the potential energy between the two electrons at a mutual distance r_{12}.

Another example is an electron in the field of a helium ion (or any other one-electron ion) with the charge Z; here we should have

$$H^\circ = \frac{1}{2m}\left(\frac{h}{2\pi i}\right)^2\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right) - \frac{(Z-1)e^2}{r},$$
$$H' = -\exp\left[-2Z(r/\alpha_H)\right]\left(\frac{1}{r} + \frac{Z}{a_H}\right), \tag{39.3}$$

The unperturbed energy H° then corresponds to the field of a reduced nuclear charge $(Z-1)e$; while H' represents the field from the remaining charge e, together with the statistically distributed electron charge $-e$.

We shall, in the following, employ the general notation

$$(H - E)\psi = 0, \qquad H = H^\circ + H', \tag{39.4}$$

for all kinds of eigenvalue problems. By means of suitable transformations of the coordinates and the parameter E, the differential equation corresponding to the operators (39.3) may, for instance, be reformulated as

$$\left[\frac{d^2}{dx^2} + \frac{\lambda}{4} + \frac{Z-1}{x} + e^{-2x}\left(\frac{1}{x} + 1\right)\right]y = 0, \qquad y = x\psi. \tag{39.5}$$

This may, in turn, be rewritten as

$$\left(H - \frac{\lambda}{4}\right)y = 0, \qquad H = H^\circ + H',$$
$$H^\circ = -\frac{d^2}{dx^2} - \frac{Z-1}{x}, \qquad H' = -e^{-2x}\left(\frac{1}{x} + 1\right). \tag{39.6}$$

In order to keep our exposition on a reasonably simple formal level, we shall henceforth assume that the operator H is always given in self-adjoint form; this is the reason for choosing $y = x\psi$ as the dependent variable in (39.5). In the equation for the original (radial) wave function we should have had to put

$$H^\circ = -\frac{d}{dx}x^2\frac{d}{dx} - (Z-1)x. \tag{39.7}$$

Perturbation of Discrete Eigenvalues

For simplicity we assume that the solutions of the equation $(H^\circ - E)\psi = 0$ are known, and that its eigenvalues constitute a discrete spectrum E_1°,

$E_2^\circ, \cdots, E_n^\circ, \cdots$. We then have

$$\begin{aligned}(H^\circ - E_n^\circ)\psi_n &= 0,\\ (H^\circ - E_m^\circ)\psi_m &= 0,\end{aligned} \tag{39.8}$$

and it may be shown, in the usual way, that ψ_n and ψ_m are orthogonal, so that we may put

$$\int \psi_n \psi_m \, d\tau = \delta_{nm}, \tag{39.9}$$

where $d\tau$ is the element of volume in the coordinate space.

In order to solve the equation

$$(H - E)\psi = 0 \qquad \text{or} \qquad (H^\circ - E)\psi + H'\psi = 0 \tag{39.10}$$

we now write

$$\psi = \sum_m c_m \psi_m. \tag{39.11}$$

The substitution of this in (39.11) then yields

$$\sum_m c_m (E_m^\circ - E + H')\psi_m = 0. \tag{39.12}$$

The unperturbed eigenfunctions ψ_n may in general be taken to constitute a complete set; consequently we may express $H'\psi_m$ in terms of these functions as

$$\begin{aligned}H'\psi_m &= \sum_n H'_{nm}\psi_n,\\ H'_{nm} &= \int \psi_n H' \psi_m \, d\tau.\end{aligned} \tag{39.13}$$

Hence (39.12) may be written

$$\sum_n \psi_n \sum_m [(E_m^\circ - E)\,\delta_{nm} + H'_{nm}]c_m = 0. \tag{39.14}$$

Since all the ψ_n are linearly independent, it follows that

$$\sum_m [(E_m^\circ - E)\,\delta_{nm} + H'_{nm}]c_m = 0, \tag{39.14a}$$

This is a homogeneous set of equations in the unknown expansion coefficients c_m. In order to have a solution the corresponding determinant must be zero; thus

$$\begin{vmatrix} E_1^\circ - E + H'_{11} & H'_{12} & H'_{13} \cdots \\ H'_{12} & E_2^\circ - E + H'_{22} & H'_{23} \cdots \\ H'_{13} & H'_{23} & E_3^\circ - E + H'_{33} \cdots \\ \cdot & & \\ \cdot & & \\ \cdot & & \end{vmatrix} = 0. \tag{39.15}$$

By means of this determinantal equation, all the eigenvalues E_n may be determined; the difference between these and the original eigenvalues E_n° then furnishes the perturbations of the eigenvalues, or the perturbation energy of each state.

First- and Second-Order Perturbation

Let us, for a moment, revert to the form (39.1*a*) of our eigenvalue problem; the parameter ε, which may be assumed large or small, will then make it easier for us to keep track of the order of magnitude of the several perturbation terms. If ε is fairly small, the terms appearing in our equations will be expandable in rapidly converging series in powers of ε. Thus, for instance, the energy of the nth quantum state may be written as

$$E_n = E_n^\circ + \varepsilon E_n' + \varepsilon^2 E_n'' + \varepsilon^3 E_n''' + \cdots . \tag{39.16}$$

We now take as our starting point the unperturbed state ψ_n corresponding to $c_n = 1$, $c_m = 0$ for $m \neq n$. In the perturbed state the coefficients c_m will then be of order ε, and we may rewrite (39.14*a*) in the form corresponding to (39.1*a*), that is,

$$\sum_m [(E_m^\circ - E)\,\delta_{nm} + \varepsilon H'_{nm}]c_m = 0. \tag{39.17}$$

In this nth equation all off-diagonal terms will be of order ε^2; if these are disregarded for the moment, we obtain

$$E_n^\circ - E + \varepsilon H'_{nn} = 0, \tag{39.18}$$

and the approximate perturbed energy for the nth state

$$E_n = E_n^\circ + \varepsilon H'_{nn}. \tag{39.19}$$

It follows from (39.13) that this first-order perturbation of the energy may be calculated by means of the unperturbed function ψ_n alone.

In order to proceed we must now also take into account the remaining equations, say, the nth. Here, similarly, all terms are of the order ε^2, except the diagonal term $m = n'$, and the nth term. These are of the order ε, the diagonal term because of the coefficient c_n, and the nth term (with $c_n = 1$) because it contains only the perturbation $\varepsilon H'_{n'n}$. To the first order in ε we then obtain the equation

$$(E_m^\circ - E + \varepsilon H'_{mm})c_m + \varepsilon H'_{mn}c_n = 0, \tag{39.20}$$

where n' has been replaced by m. Since (by assumption) $c_n = 1$, this yields

$$c_m = \frac{\varepsilon H'_{mn}}{E_n^\circ - E_m^\circ + \varepsilon(H'_{nn} - H'_{mm})}, \tag{39.21}$$

where the value (39.19) of E_n has been substituted for E. Instead of putting

$c_m = 0$, as before, we now substitute these first-order values in the nth equation (39.17); this leads to a more accurate expression for the energy,

$$E_n = E_n^\circ + \varepsilon H'_{nn} + \sum_m{}' \frac{\varepsilon^2 H'_{nm} H'_{mn}}{E_n^\circ - E_m^\circ + \varepsilon(H'_{nn} - H'_{mm})}. \tag{39.22}$$

The dashed summation sign signifies that the case $m = n$ is to be excluded from the summation.

Equation 39.22 yields not only the first- and second-order, but even the third-order perturbation of the energy; if the denominator of the sum in (39.22) is expanded, a term of the order ε^3 is obtained which contains the complete third-order perturbation.

We have assumed in the above considerations that the eigenfunctions are real. This may be done if no energy levels coincide—or to express it differently—if there corresponds only one solution to each energy value. If two or more energy levels coincide, we say that degeneracy is present. In general, however, we must assume that the eigenfunctions are complex. Even for single levels, these functions will be complex if the time factors $\exp[(2\pi i/h)E_n t]$ are taken into account. Moreover, any eigenfunctions may be multiplied by an arbitrary complex number. Hence we ought in general to consider complex eigenfunctions and their complex conjugates. In terms of these, the matrix elements in the preceding equations are defined by

$$H'_{nm} = \int \psi_n^* H' \psi_m \, d\tau = (H'_{mn})^*. \tag{39.23}$$

With the form chosen in (39.22) this equation will be valid also for complex ψ_n. The only difference is that, whereas we previously (with $H'_{nm} = H'_{mn}$) could have put $(H'_{nm})^2$ in the numerator, we must now write $|H'_{nm}|^2$ which is equal to $H'_{nm} H'_{mn}$ by (39.23).

Application of the Perturbation Theory. The Harmonic Oscillator

As an example we have chosen the harmonic oscillator, since we here know the exact solution and the corresponding energy or energy parameter.

Let us choose units such that the Hamiltonian for the oscillator may be written

$$H^\circ = -\frac{d^2}{dx^2} + x^2, \qquad E_n^\circ = 2n + 1, \qquad -\infty \leqq x \leqq \infty. \tag{39.24}$$

We now choose a perturbation

$$H' = 2ax \tag{39.25}$$

which yields the total Hamiltonian

$$H = -\frac{d^2}{dx^2} + (x + a)^2 - a^2. \tag{39.26}$$

This means that the perturbed energy levels are

$$E_n = 2n + 1 - a^2 \tag{39.27}$$

which may be described as a horizontal displacement (without any change of shape) of the parabola for the potential energy through an interval $-a$, and a similar vertical (downward) displacement $-a^2$, with a corresponding lowering of the energy levels.

What we now need is a determination of the matrix elements H'_{mn} or x_{mn}. It follows from the definition of adjoint operators that we may write

$$Q_{n,n+1} = (m\omega q + ip)_{n,n+1} = Q^*_{n+1,n} = (m\omega q - ip)_{n+1,n}, \tag{39.28}$$

while all other matrix elements, including $Q_{n+1,n}$ and $Q^*_{n,n+1}$, vanish. The two matrix elements (39.28) were earlier found to be

$$\begin{aligned} Q_{n,n+1} &= Q^*_{n+1,n} = [2m\hbar\omega(n + 1)]^{1/2}, \\ Q^*_{n,n+1} &= Q_{n+1,n} = 0. \end{aligned} \tag{39.29}$$

Compare (31.15). This yields

$$\begin{aligned} q_{n+1,n} &= q_{n,n+1} = \left(\frac{\hbar}{m\omega}\right)^{1/2}\left(\frac{n + 1}{2}\right)^{1/2}, \\ -ip_{n+1,n} &= ip_{n,n+1} = (m\hbar\omega)^{1/2}\left(\frac{n + 1}{2}\right)^{1/2}. \end{aligned} \tag{39.30}$$

The Hamiltonian (39.24) corresponds to the specific units $m = 1$, $\omega = 1$, $\hbar = \dfrac{h}{2\pi} = 1$, and to the double energy function. In this case we obtain the matrix elements

$$x_{n+1,n} = x_{n,n+1} = \left(\frac{n + 1}{2}\right)^{1/2}, \tag{39.31}$$

and

$$\left(\frac{d}{dx}\right)_{n+1,n} = -\left(\frac{d}{dx}\right)_{n,n+1} = \left(\frac{n + 1}{2}\right)^{1/2}. \tag{39.32}$$

We now perform a wave-mechanical analytic determination of the x-matrix elements. Writing

$$\psi_n = N_n \exp(-\tfrac{1}{2}x^2)H_n(x) \tag{39.33}$$

and substituting in the equation $H^\circ\psi_n = E_n^\circ\psi_n$, we find

$$\left(-\frac{d^2}{dx^2} + 2x\frac{d}{dx} - 2n\right)H_n(x) = 0 \tag{39.34}$$

which is the differential equation for the well-known Hermite polynomials. Splitting off a factor $e^{x^2/2}$ in ψ_n, we may also write (39.34) as

$$\left[-\frac{d^2}{dx^2} - 2x\frac{d}{dx} - (2n+2)\right]e^{-x^2}H_n(x) = 0. \tag{39.35}$$

The calculation

$$\int_{-\infty}^{\infty} e^{-x^2}H_n^{\,2}(x)\,dx = (-1)^n\int_{-\infty}^{\infty} H_n(x)\frac{d^n}{dx^n}e^{-x^2}\,dx = 2^n n!\sqrt{\pi} \tag{39.36}$$

then yields the normalization factor in (39.32),

$$N_n = (2^n n!\sqrt{\pi})^{-1/2}, \tag{39.37}$$

By means of the recursive formula

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x) \tag{39.38}$$

we may express $xH_n(x)$ in terms of $H_{n+1}(x)$ and $H_{n-1}(x)$; the coefficient of $H_{n+1}(x)$ is then evidently $\frac{1}{2}$. Similarly $x\psi_n$ may be expressed in terms of ψ_{n+1} and ψ_{n-1}; and the coefficient of ψ_{n+1} is then, as in (39.31), given as

$$x_{n+1,n} = \frac{1}{2}\frac{N_n}{N_{n+1}} = \left(\frac{n+1}{2}\right)^{1/2}. \tag{39.39}$$

We may now write our determinantal equation

$$\begin{vmatrix}
\cdots & & \cdots & \cdots & \cdots \\
\cdots & 2n-1-E & 2a\left(\frac{n}{2}\right) & 0 & \cdots \\
\cdots & 2a\left(\frac{n}{2}\right) & 2n+1-E & 2a\left(\frac{n+1}{2}\right) & \cdots \\
\cdots & 0 & 2a\left(\frac{n+1}{2}\right) & 2n+3-E & \cdots \\
\cdots & & & & \\
\cdot & & & & \\
\cdot & & & & \\
\cdot & & & &
\end{vmatrix} = 0. \tag{39.40}$$

It follows from (39.18) that $E_n' = 0$. In the expression for the third-order perturbation of the energy the factor $H'_{mn}H'_{nn}H'_{nm}$ appears. Hence $E_n''' = 0$ also; this applies for all perturbation terms of odd order. Thus, as was to be expected, the energy is a function of a^2. It follows from (39.22) that the

second-order term is

$$E_n'' = 2a^2(|x_{n,n-1}|^2 - |x_{n+1,n}|^2) = -a^2. \tag{39.41}$$

Clearly the second-order perturbation provides an exhaustive result; whence we must conclude that $E_n^{(4)} = E_n^{(6)} = \cdots = 0$, although this cannot be explicitly shown by means of our limited considerations.

We might have chosen a different form of the perturbation function, namely,

$$H' = (2a + a^2)x^2, \tag{39.42}$$

and thus obtained

$$H = -\frac{d^2}{dx^2} + (1 + a)^2x^2, \tag{39.43}$$

$$E_n = (2n + 1)(1 + a).$$

This may be described as a progressive raising of the energy levels with $(2a + 1)a$, due to the more narrow shape of the potential energy parabola.

Here, however, the perturbation parameter is

$$\varepsilon = 2a + a^2 \tag{39.44}$$

which yields

$$a = (1 + \varepsilon)^{1/2} - 1 = \tfrac{1}{2}\varepsilon - \tfrac{1}{8}\varepsilon^2 + \tfrac{1}{16}\varepsilon^3 - \cdots, \tag{39.45}$$

$$E_n' = \tfrac{1}{2}\varepsilon(2n + 1), \qquad E_n'' = -\tfrac{1}{8}\varepsilon(2n + 1), \qquad E_n''' = \tfrac{1}{16}\varepsilon^3(2n + 1). \tag{39.46}$$

The matrix elements of x^2 may be found by matrix multiplication,

$$\begin{aligned}(x^2)_{nn} &= x_{n,n+1}x_{n+1,n} + x_{n,n-1}x_{n-1,n} = \tfrac{1}{2}(2n + 1),\\ (x^2)_{n+2,n} &= x_{n+2,n+1}x_{n+1,n} = \tfrac{1}{2}[(n + 1)(n + 2)]^{1/2},\\ (x^2)_{n-2,n} &= x_{n-2,n-1}x_{n-1,n} = \tfrac{1}{2}[(n - 1)n]^{1/2}.\end{aligned} \tag{39.47}$$

It is immediately clear that the resulting expression for E_n' agrees with (39.46). This is also the case for the second- and third-order perturbations; we find that

$$E_n'' = \frac{\varepsilon^2}{16}[(n - 1)n - (n + 1)(n + 2)] = -\frac{\varepsilon^2}{8}(2n + 1), \tag{39.48}$$

$$\begin{aligned}E_n''' &= \frac{1}{16}[-H_{nn}'(H_{n,n+2}'^2 + H_{n,n-2}'^2) + H_{n+2,n+2}'H_{n,n+2}'^2 + H_{n-2,n-2}'H_{n,n-2}'^2]\\ &= \frac{\varepsilon^3}{16}\left\{\frac{1}{8}(2n + 1)[(n + 1)(n + 2) + (n - 1)n] + \frac{1}{8}(2n + 5)(n + 1)\right.\\ &\qquad \left.\times (n + 2) + \frac{1}{8}(2n - 3)(n - 1)n\right\} \qquad (39.49)\\ &= \frac{\varepsilon^2}{16}\left[\frac{1}{2}(n + 1)(n + 2) - \frac{1}{2}(n - 1)n\right] = \frac{\varepsilon^3}{16}(2n + 1).\end{aligned}$$

Problems

1. Consider the eigenvalue problem $(H - \lambda)y = 0$, with

$$H = H^\circ + H', \qquad H^\circ = -\frac{d}{dx}x\frac{d}{dx} + \frac{x}{4}, \qquad H' = e^{-x}.$$

Show that the unperturbed problem has solutions for $\lambda = \lambda_n = n + \frac{1}{2}$, $n = 0, 1, \cdots$, and that these solutions may be written as

$$y_n = e^{-(x/2)}\overline{L}_n(x),$$

where the $\overline{L}_n(x)$ are nth-degree polynomials.

2. Write the differential equation for y_n and y_m, and show that

$$\int_0^\infty y_n y_m\, dx = 0, \qquad \text{when} \qquad m \neq n.$$

3. Defining a set of functions by

$$\psi(x, s) = \frac{\exp\left(-\frac{x}{2}\frac{1+s}{1-s}\right)}{1-s} = \sum_{n=0}^{\infty} y_n(x)s^n,$$

show that we obtain the same result as in Problem 2 for the integral

$$\int_0^\infty \psi(x, s)\psi(x, t)\, dx.$$

Show that the functions y_n are mutually orthonormalized, that is, that

$$\int_0^\infty y_n y_m\, dx = \delta_{nm}.$$

4. The first eigenfunction is $y_0 = e^{-(x/2)}$ Show, by means of the definition in Problem 3, that

$$H'_{n0} = (\tfrac{1}{2})^{n+1}.$$

5. Use this to calculate the second-order perturbation in λ, and show that it is equal to $-\frac{1}{4} \cdot \log \frac{3}{4}$.

40. PERTURBATION PROBLEMS TREATED BY VARIATIONAL METHODS

Extremal Properties of the Eigenvalues

By means of variational calculus we may define the eigenvalues for the energy as extremal or stationary values of the expression

$$E = \frac{\int \psi H \psi\, d\tau}{\int \psi^2\, d\tau}, \tag{40.1}$$

assuming for simplicity that the eigenfunctions are real and the eigenvalues single. The condition for extremal or stationary values of E may be written, symbolically, as

$$\frac{\delta E}{\delta \psi} = 0, \tag{40.2}$$

meaning that the variation of E resulting from a variation $\delta\psi$ of ψ is to be small of the order $(\delta\psi)^2$ if ψ is the solution of the problem. Writing

$$\psi = \sum_n c_n \psi_n, \tag{40.3}$$

where ψ_n is a set of orthonormal functions, we thus have

$$E = \frac{\Sigma_{nm} H_{nm} c_n c_m}{\Sigma_n c_n^2} = \text{extr.} \tag{40.4}$$

Furthermore if we write

$$H = H^\circ + H', \qquad H^\circ \psi_n = E_n^\circ \psi^\circ, \tag{40.5}$$

so that the auxiliary functions ψ_n are solutions of the corresponding unperturbed eigenvalue problem, we obtain

$$E = \frac{\Sigma_n E_n^\circ c_n^2 + \Sigma_{nm} H'_{nm} c_n c_m}{\Sigma_n c_n^2}. \tag{40.6}$$

The condition for stationary values of E with respect to variation of the coefficients c_n may now be expressed as

$$\frac{\partial E}{\partial c_n} = 0; \tag{40.7}$$

this is easily seen to lead to the set of equations (39.14*a*).

Other Formulations of the Variation Problem

We write (40.1) in the form

$$\int \psi(H - E)\psi \, d\tau = 0. \tag{40.8}$$

Let us now assume that the first-order variation of E vanishes for the variations $\delta\psi$, that is, $\delta E = 0$ or $\delta E/\delta\psi = 0$. Since H is self-adjoint, we have

$$\int \psi H \delta\psi \, d\tau = \int \delta\psi H\psi \, d\tau.$$

Consequently the condition for stationarity of E with respect to the variation of ψ in (40.8) may be written, after cancellation of a factor 2, as

$$\int \delta\psi(H - E)\psi \, d\tau = 0. \tag{40.9}$$

Since $\delta\psi$ is completely arbitrary, the well-known differential equation $(H - E)\psi = 0$ follows. Equation 40.9 however, may also be utilized in a more direct fashion. We may choose a complete orthonormalized set ψ_n and perform successive variations $\delta\psi = \varepsilon\psi_1, \varepsilon\psi_2, \cdots, \varepsilon\psi_n$, where the ε signifies only that the variations are to be small. The cancellation of ε leads to a set of equations

$$\int \psi_n(H - E)\psi \, d\tau = 0. \tag{40.10}$$

Writing

$$\psi = \sum_m c_m\psi_m, \tag{40.11}$$

we thus obtain the linear system of equations

$$\sum_m (H_{nm} - E\,\delta_{nm})c_m = 0. \tag{40.12}$$

If we now assume that the ψ_n are eigenfunctions for the operator H°, that $H^\circ_{nm} = 0$ when $m \neq n$ and $H^\circ_{nn} = E^\circ_n$, we arrive back at the linear system of (39.14*a*) by putting $H = H^\circ + H'$.

Approximations in Direct Calculation

Let us consider the equation

$$(H^\circ - E + \varepsilon H')\psi = 0 \tag{40.13}$$

and expand ψ and E in powers of ε,

$$\begin{aligned} \psi &= \psi_0 + \varepsilon\psi_1 + \varepsilon^2\psi_2 + \cdots, \\ E &= E^\circ + \varepsilon E' + \varepsilon^2 E'' + \cdots. \end{aligned} \tag{40.14}$$

Putting successive powers of ε equal to zero, we thus obtain

$$(H^\circ - E^\circ)\psi_0 = 0, \tag{40.15}$$

$$(H^\circ - E^\circ)\psi_1 + (H' - E')\psi_0 = 0, \tag{40.15a}$$

$$(H^\circ - E^\circ)\psi_2 + (H' - E')\psi_1 - E''\psi_0 = 0, \tag{40.15b}$$

and

$$(H^\circ - E^\circ)\psi_3 + (H' - E')\psi_2 - E''\psi_1 - E''''\psi_0 = 0. \tag{40.15}$$

We now assume that ψ_0 and E° are known and (for simplicity) that

$$\int \psi_0^2 \, d\tau = 1. \tag{40.16}$$

Multiplying (40.15) by ψ_1 and (40.15*a*) by ψ_0, subtracting and integrating, we then find

$$E' = \int \psi_0 H' \psi_0 \, d\tau. \tag{40.17}$$

Thus we see once again that the first-order perturbation of the energy may be determined by means of the unperturbed function ψ_0.

A similar treatment of (40.15) and (40.15*b*) yields

$$E'' = \int \psi_0 (H' - E') \psi_1 \, d\tau. \tag{40.18}$$

Hence the determination of the second-order energy perturbation requires knowledge of the first-order perturbation of the wave function. Equation (40.18) may also be written

$$E'' = \int \psi_0 H' \psi_1 \, d\tau, \qquad \int \psi_0 \psi_1 \, d\tau = 0, \tag{40.18a}$$

since we may always by (40.15*a*) add a term $c\psi_0$ and determine c such that ψ_0 and ψ_1 become mutually orthogonal. This is, however, a minor detail.

Finally we may multiply (40.15*c*) by ψ_0 and (40.15) by ψ_3, and then subtract and integrate to obtain

$$E''' = \int [\psi_0 (H' - E') \psi_2 - E'' \psi_0 \psi_1] \, d\tau. \tag{40.19}$$

This equation apparently indicates that we must know ψ_2 in order to calculate E''''. However, we may deduce from (40.15*a*) and (40.15*b*), by a process similar to that mentioned above, the relation

$$0 = \int [\psi_1 (H' - E') \psi_1 - \psi_2 (H' - E') \psi_0 - E'' \psi_1 \psi_0] \, d\tau. \tag{40.19a}$$

The addition of (40.19) and (40.19*a*) then yields

$$E''' = \int \psi_1 (H' - E') \psi_1 \, d\tau - 2E'' \int \psi_1 \psi_0 \, d\tau. \tag{40.19b}$$

It follows that the calculation of the third-order energy perturbation requires a knowledge of only the first-order perturbation of the wave function. This is a general rule: Each new approximation of the wave function brings us two steps ahead in the calculation of the energy, all in powers of the perturbation parameter ε.

General Formulation of the Variational Perturbation Expansion

Let us consider, once more, the equation

$$(H^\circ - E - \varepsilon H') \Phi = 0, \tag{40.20}$$

and expand the energy E of the system and its complete state function Φ as follows:

$$E = \sum_{n=0}^{\infty} \varepsilon^n E_n, \tag{40.21}$$

$$\Phi = \sum_{n=0}^{\infty} \varepsilon^n \varphi_n, \tag{40.22}$$

As in (40.3) we here write the nth order perturbation in the trial function φ_n as a linear combination of m terms taken from some complete basis or set of functions

$$\varphi_n = \sum_{i=1}^{m} c_{ni} \psi_i. \tag{40.23}$$

For brevity we introduce the notation

$$H^\circ_{mn} = \int \varphi_m H^\circ \varphi_n \, d\tau, \qquad N_{mn} = \int \varphi_m \varphi_n \, d\tau. \tag{40.24}$$

The general expression for the perturbation equations (40.15) of the system then takes the form

$$H^\circ \varphi_n + H' \varphi_{n-1} - \sum_{k=0}^{n} E_n \varphi_{n-k} = 0, \tag{40.25}$$

where only terms with positive indices are to be included.

We shall now assume the function φ_0 to be known, and attempt to determine the remaining functions φ_n by a variational method.

We already know that the wave function for any discrete atomic state is characterized by the fact that it yields a stationary value for the expression (40.1). This is equivalent to demanding that the expression

$$\int \Phi H \Phi \, d\tau - E \int \Phi\Phi \, d\tau \tag{40.26}$$

be stationary, with the additional condition that the norm $\int \Phi\Phi \, d\tau$ remain constant during the variation. The latter leads to the orthogonality relations

$$\sum_{k=0}^{n} N_{k,n-k} = 0, \qquad n = 1, 2, 3, \cdots. \tag{40.27}$$

Let us now substitute (40.21) and (40.22) into (40.26), and require that it be stationary for all values of ε; moreover we assume that all functions φ_k, $k \leqq n - 1$, have already been found. We then find that the nth order perturbation function φ_n is uniquely determined by the requirement that the expression

$$F_n(E, 0) \equiv H^\circ_{nn} + 2H'_{n-1,n} - \sum_{p=0}^{2n-1} E_p \sum_{k=n-p}^{n} N_{2n-p-k,k} \tag{40.28}$$

be stationary with respect to variations of φ_n.

This leads to the set of equations

$$\int \psi_i H^\circ \varphi_n \, d\tau + \int \psi_i H' \varphi_{n-1} \, d\tau - \sum_{p=0}^{n} E_p \int \psi_i \varphi_{n-p} \, d\tau = 0, \tag{40.29}$$

where $i = 1, 2, 3, \cdots, m$.

The solution of this set of linear equations is the best approximation—to the nth order perturbation in the wave function—obtainable by means of the m terms from the chosen set of basis functions. This solution is then substituted into the equation

$$F_n(E, 0) = 0, \tag{40.30}$$

and we obtain successively, using the relations (40.23), (40.27) and (40.29), the following expressions for the energy coefficients

$$\int \psi_i H^\circ \varphi_2 \, d\tau + \int \psi_i H' \varphi_1 \, d\tau - \int (E_0 \psi_i \varphi_2 + E_1 \psi_i \varphi_1 + E_2 \psi_i \varphi_2) \, d\tau = 0;$$

that is

$$E_2 N_{00} = H^\circ_{02} + H'_{01} - E_0 N_{02} - E_1 N_{01} = H'_{01} - E_1 N_{01}. \tag{40.31}$$

$$\begin{aligned} E_3 N_{00} &= H^\circ_{03} + H'_{02} - E_0 N_{03} - E_1 N_{02} - E_2 N_{01} \\ &= -H^\circ_{12} + E_0 N_{12} - E_2 N_{01} \\ &= H'_{11} - E_1 N_{11} - E_2 N_{10} - E_2 N_{01} \\ &= H'_{11} - E_1 N_{11}. \end{aligned} \tag{40.32}$$

$$\begin{aligned} E_4 N_{00} &= H^\circ_{04} + H'_{03} - E_0 N_{04} - E_1 N_{03} - E_2 N_{02} - E_3 N_{01} \\ &= -H^\circ_{13} + E_0 N_{13} - E_2 N_{02} - E_3 N_{01} \\ &= H'_{12} - E_1 N_{12} - E_2 N_{11} - E_3 N_{10} - E_2 N_{02} - E_3 N_{01} \\ &= H'_{12} - E_1 N_{12} - E_2 (N_{11} + N_{02}). \end{aligned} \tag{40.33}$$

Thus having found the approximation function by means of the set of equations (40.29), we obtain the general formulas for the determination of the energy coefficients E_{2n} and E_{2n+1},

$$E_0 = H^\circ_{00}, \qquad E_1 = H'_{00}, \tag{40.34}$$

$$E_{2n} = H'_{n-1,n} - \sum_{k=1}^{n} E_k \sum_{i=0}^{k-1} N_{n-k+i,n-i}, \tag{40.35}$$

and

$$E_{2n+1} = H'_{n,n} - \sum_{k=1}^{n} E_k \sum_{i=0}^{k-1} N_{n-k+1+i,n-i}, \qquad n \geqq 1; \tag{40.36}$$

it is here assumed that the zeroth order function φ_0 has been normalized.

Problems

1. Consider, once again, Problem 1 of Section 39, but substitute $\varepsilon H' = \varepsilon e^{-x}$ for $H' = e^{-x}$. Show that

$$(H^\circ - \lambda^\circ)y_0 = 0$$

has the solutions $\lambda^\circ = \frac{1}{2}$, $y_0 = e^{(-x/2)}$. Calculate the first-order perturbation of λ in the equation $(H - \lambda)y = 0$, $\lambda = \lambda^\circ + \varepsilon\lambda' + \varepsilon^2\lambda'' + \cdots$, and show that it is $\lambda' = \frac{1}{2}$.

2. Calculate y_1 from the equation

$$(H^\circ - \lambda^\circ)y_1 + (H' - \lambda')y_0 = 0,$$

and show that

$$y_1 = \frac{1}{2}e^{-(x/2)}\int_0^x \frac{1 - e^{-x}}{x}\,dx.$$

3. Utilize this result and (40.18) to find λ'' in the above expansion; show that

$$\lambda'' = -\frac{1}{4}\int_0^\infty \frac{e^{-x}(1 - e^{-x})^2}{x}\,dx.$$

41. PERTURBATION OF DEGENERATE STATES

Examples of Degeneracy

The most obvious example of quantum-mechanical degeneracy is furnished by the hydrogen atom and its homologous ions He^+, Li^{++}, and so forth. A state with the energy

$$E_n = -\frac{Z^2Rh}{n^2} \tag{41.1}$$

is composed of no less than n^2 linearly independent states. Previously we have seen how this compound state may be split into well-defined individual states, by quantization of two particular dynamic variables, apart from the energy function H: namely, the total angular momentum $|\mathbf{m}|$ (or its square $\mathbf{m}^2$) and its component along one of the axes, for example, m_z. These new dynamic variables have the quantum numbers $l = 0, 1, \cdots, n - 1$ and $m = -l, \cdots, 0, \cdots, l$, commonly referred to as the azimuthal and magnetic quantum numbers. The eigenfunctions may, in this case, be written as

$$\psi_{nlm} = R_{nl}(r)P_l^m(\cos\vartheta)e^{im\varphi}. \tag{41.2}$$

In general, however, we may regard any n^2 linear combinations of these functions as belonging to the eigenvalue (41.1). We shall see later how a certain group of this kind splits very naturally into definite eigenfunctions when perturbing forces are introduced.

Another interesting example is that of the symmetric and antisymmetric wave functions for two electrons. Disregarding the interaction energy e^2/r_{12} between them, we shall have, for an eigenvalue

$$E_{n_1 n_2} = -Z^2 Rh\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right), \tag{41.3}$$

equivalent solutions

$$\begin{aligned} \psi &= \psi_{n_1}(1)\psi_{n_2}(2), \\ \bar{\psi} &= \psi_{n_2}(1)\psi_{n_1}(2). \end{aligned} \tag{41.4}$$

of the wave equation; ψ_{n_1} and ψ_{n_2} are assumed to be of the form (41.2). In addition to the degeneracy described above, then, (41.4) represents a new kind of degeneracy which simply arises from the fact that the particles have identical properties. If the interaction energy e^2/r_{12} is introduced and the corresponding first-order perturbation calculated, this degeneracy disappears and we obtain two solutions, namely,

$$\psi_s = \psi + \bar{\psi}, \qquad \psi_a = \psi - \bar{\psi}. \tag{41.5}$$

The former is symmetric, and the latter antisymmetric, in the coordinates of the two electrons.

In connection with such questions of symmetry it is useful to note that there exist in quantum mechanics other quantizable operators than those that represent dynamic variables in the usual physical sense: analytic functions of coordinates and momentum components.

An example of an operator of a completely different sort is the permutation operator P_{12}, defined by

$$P_{12}\psi(1, 2) = \psi(2, 1); \tag{41.6}$$

its effect on a state function is to exchange the coordinates of two particles. For a symmetric operator, such as the energy function H, it is easily seen that

$$HP_{12}\psi(1, 2) = H\psi(2, 1) = P_{12}H\psi(1, 2), \tag{41.7}$$

or more briefly,

$$HP_{12} = P_{12}H. \tag{41.7a}$$

This means by general rules that the permutation operator P_{12} may be quantized simultaneously with the energy.

It is now a consequence of (41.6) that

$$\begin{aligned} P_{12}^2\psi(1, 2) &= P_{12}\psi(2, 1) = \psi(1, 2), \\ \text{i.e.} \qquad P_{12}^2 &= 1. \end{aligned} \tag{41.8}$$

Hence the only possible eigenvalue for the permutation operator is

$$P_{12} = \pm 1. \tag{41.9}$$

This means that all solutions of a wave equation for two electrons—after the degeneracy has been canceled by means of the interaction $e^2{}_x r_{12}$—are either symmetric or antisymmetric,

$$\begin{aligned} P_{12}\psi_s(1,2) &= \psi_s(1,2), & \psi_s(2,1) &= \psi_s(1,2), \\ P_{12}\psi_a(1,2) &= -\psi_a(1,2), & \psi_a(2,1) &= -\psi_a(1,2). \end{aligned} \tag{41.10}$$

It follows from these considerations that the simplest procedure for splitting degenerate states by means of a given perturbation is quite often that of finding a new operator that corresponds to or is connected with the perturbation operator, and which (if possible) commutes with H, so that it may be quantized. We may not, however, assume that this is always possible; hence we shall indicate briefly the general procedure for the treatment of such problems.

First-Order Perturbation of Degenerate States

Let us assume that we have, for an unperturbed system, N solutions of the equations

$$(H^\circ - E^\circ)\psi = 0; \tag{41.11}$$

these solutions will be denoted by $\psi_1, \psi_2, \cdots, \psi_N$, and assumed to be orthonormalized. We now try to determine eigenfunctions and eigenvalues for a system with the Hamiltonian $H = H^\circ + H'$ and the wave equation

$$(H - E)\Psi = 0. \tag{41.12}$$

Expanding Φ in terms of ψ_n,

$$\Psi = \sum_n c_n \psi_n, \tag{41.13}$$

and substituting in (41.12), we obtain

$$\sum_n c_n[H' - (E - E^\circ)]\psi_n = 0; \tag{41.13a}$$

multiplication by a fixed ψ_m and integration then leads to

$$\sum_n c_n[H'_{mn} - (E - E^\circ)\,\delta_{nm}] = 0. \tag{41.13b}$$

Thus we arrive at the determinantal equation

$$\begin{vmatrix} E^\circ - E + H'_{11} & H'_{12} & \cdots & H'_{1N} \\ H'_{12} & E^\circ - E + H'_{22} & \cdots & H'_{2N} \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ H'_{1N} & & & E^\circ - E + H'_{NN} \end{vmatrix} . \tag{41.14}$$

Assuming that all H'_{mn} are of the order ε, we shall not (as previously) have that the eigenvalues up to the first order in ε are given by $E_n = E^\circ + H'_{nn}$. The reason for this is that all diagonal terms are of the order of E' or ε, when $E = E^\circ + E'$ is substituted in the determinant. Hence in order to find the values of E', that is, of the first-order perturbation energy, it is necessary to solve the complete determinantal equation (41.14). The result is the energy values

$$E_n = E^\circ + E'_n. \tag{41.15}$$

Successive substitutions of these in (41.13*b*) yield the corresponding coefficients $c_m = c_{mn}$, and hence also [by means of (41.13)] the new eigenfunctions

$$\Psi_n = \sum_m c_{nm}\psi_m. \tag{41.16}$$

These functions thus become linear combinations of the original eigenfunctions for the unperturbed system.

Applications of the Theory for Perturbation of Degenerate Systems

We shall now illustrate the theory by a few examples. Since we do not wish to go into detail, we shall stick to the types of degeneracy already mentioned. Let us first consider the two-electron problem in (41.4), putting

$$\psi = \psi_1, \qquad \bar{\psi} = \psi_2. \tag{41.17}$$

The problem may then be summarized by the equations

$$\begin{gathered}(H - E)\psi = 0,\\ H = H^\circ + H', \quad H' = \frac{e^2}{r_{12}},\\ H^\circ\psi_1 = E^\circ\psi_1, \qquad H^\circ\psi_2 = E^\circ\psi_2,\end{gathered} \tag{41.18}$$

and we write

$$\psi = c_1\psi_1 + c_2\psi_2. \tag{41.18*a*}$$

For orthonormal ψ_1 and ψ_2 we then obtain

$$\begin{aligned}(E^\circ - E + H'_{11})c_1 + H'_{12}c_2 &= 0,\\ H'_{12}c_1 + (E^\circ - E + H'_{22})c_2 &= 0,\end{aligned} \tag{41.18*b*}$$

where $H'_{22} = H'_{11}$. The solutions are evidently

$$\begin{aligned}E_s &= E^\circ + H'_{11} + H'_{12}, \qquad c_1 = c_2,\\ E_a &= E^\circ + H'_{11} - H'_{12}, \qquad c_1 = -c_2.\end{aligned} \tag{41.18*c*}$$

Thus we find, as already predicted previously, a symmetric and an antisymmetric solution with a common perturbation energy H'_{11} of the usual

type. In addition, however, there appears the so-called exchange energy H'_{12} with a positive and a negative sign. The state of lowest energy is the antisymmetric.

As another example we consider a hydrogen atom in a homogeneous magnetic field of strength F which we take to be directed along the z-axis. This problem has already been discussed in the preceding chapter, Section 33, on the Zeeman effect. It was there shown [compare (33.5)] that, for $H_z = F$, an additional term appeared in the Hamiltonian; this term may be written

$$H' = \mu_0 F \frac{1}{i} \frac{\partial}{\partial \varphi}, \qquad \mu_0 = \frac{eh}{4\pi m_0 c}. \tag{41.19}$$

Consider now the unperturbed hydrogen atom, and its three eigenfunctions corresponding to the azimuthal quantum number $l = 1$ and an arbitrary fixed principal quantum number n, so that the unperturbed energy is $E^\circ = -Rh/n^2$. The three functions may be written as

$$\begin{gathered} \psi_1 = R_{n1}(r) \sin \vartheta \cos \varphi, \qquad \psi_2 = R_{n1}(r) \sin \vartheta \sin \varphi, \\ \psi_3 = R_{n1}(r) \cos \vartheta. \end{gathered} \tag{41.20}$$

For all of these we then have

$$(H^\circ - E^\circ)\psi = 0,$$

where H° is the unperturbed Hamiltonian for the hydrogen atom. We now write

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 \tag{41.21}$$

whence, since

$$H'\psi_1 = i\mu_0 F\psi_2, \qquad H'\psi_2 = -i\mu_0 F\psi_1, \qquad H'\psi_3 = 0, \tag{41.21a}$$

we obtain the set of equations

$$\begin{aligned} (E^\circ - E)c_1 - i\mu_0 F c_2 &= 0, \\ i\mu_0 F c_1 + (E^\circ - E)c_2 &= 0, \\ (E^\circ - E)c_3 &= 0. \end{aligned} \tag{41.22}$$

Putting the determinant of this set equal to zero, we find the following three eigenvalues and corresponding eigenfunctions

$$\begin{aligned} &E = E^\circ + \mu_0 F, \quad c_1 = 1, \quad c_2 = i, \quad c_3 = 0, \quad \psi = R_{n1}(r) \sin \vartheta e^{i\varphi}, \\ &E = E^\circ - \mu_0 F, \quad c_1 = 1, \quad c_2 = -i, \quad c_3 = 0, \quad \psi = R_{n1}(r) \sin \vartheta e^{-i\varphi}, \\ &E = E^\circ, \qquad\quad c_1 = 0, \quad c_2 = 0, \quad c_3 = 1, \quad \psi = R_{n1}(r) \cos \vartheta. \end{aligned} \tag{41.22a}$$

Thus the degeneracy has been removed, and we obtain the well-known complex hydrogen eigenfunctions which are quantized with respect to the z-component m_z of the angular momentum.

The Stark Effect

By this effect we mean the splitting of atomic energy levels in an electric field. The Stark effect is, from an experimental point of view, more prominent than the Zeeman effect, since it becomes noticeable even for moderate electric fields, while the other requires rather strong magnetic fields in order to be measurable. However, the theoretical treatment of the Stark effect is somewhat more involved than that of the Zeeman effect; since the latter is of much greater importance for the classification of atomic spectra, it is natural that the former plays a somewhat secondary role in the theoretical treatment of atomic problems. It will not be altogether omitted here, but we shall content ourselves with discussing the so-called first-order effect in order to make the exposition as brief as possible. The so-called second-order Stark effect, which is proportional to the square of the electric field strength and is the only effect appearing for certain atomic states, is also of some interest; however, it necessitates the calculation of a second-order perturbation which would take us too far afield.

The equation of a parabola with apex ξ and focal point at the origin is in polar coordinates:

$$r = \frac{2\xi}{1 + \cos\vartheta}. \tag{41.23}$$

(See Fig. 6-1.)

Correspondingly for a parabola with apex $-\eta$, we have

$$r = \frac{2\eta}{1 - \cos\eta}. \tag{41.23a}$$

Hence we obtain the coordinate transformations

$$\begin{aligned} 2\xi &= r + z, \\ 2\eta &= r - z \end{aligned} \tag{41.24}$$

or

$$\begin{aligned} r &= \xi + \eta, \\ z &= \xi - \eta, \\ x^2 + y^2 &= 4\xi\eta \end{aligned} \tag{41.24a}$$

or

$$x = 2\sqrt{\xi\eta}\cos\varphi, \qquad y = 2\sqrt{\xi\eta}\sin\varphi, \qquad z = \xi - \eta. \tag{41.24b}$$

For the operator ∇^2 we may then deduce the expression

$$\nabla^2 = \frac{1}{\xi + \eta}\left[\frac{\partial}{\partial\xi}\xi\frac{\partial}{\partial\xi} + \frac{\partial}{\partial\eta}\eta\frac{\partial}{\partial\eta} + \left(\frac{1}{4\xi} + \frac{1}{4\eta}\right)\frac{\partial^2}{\partial\varphi^2}\right]. \tag{41.25}$$

The potential energy of an electron in a homogeneous electric field $\mathbf{E} = \mathbf{k}F$ in the z-direction is

$$V' = Fez = Fe(\xi - \eta). \tag{41.26}$$

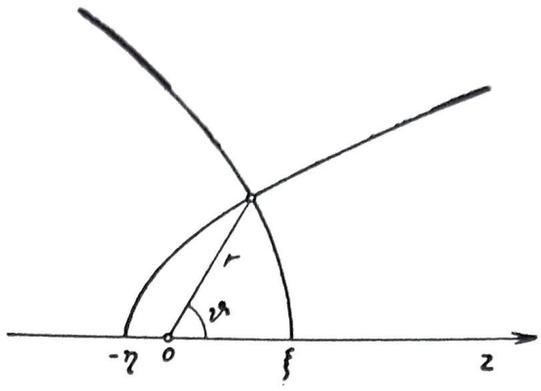

Fig. 6-1. Parabolic Coordinates

The wave equation for a one-electron atom with the nuclear charge Z may now be written

$$\left(\nabla^2 - \frac{Z^2}{n^2 a_H{}^2} + \frac{2Z}{a_H r} - \frac{2F}{e a_H} z\right)\psi = 0,$$
$$E = -\frac{Z^2 Rh}{n'^2}, \qquad n' \approx n. \tag{41.27}$$

Choosing $n'a_H/2Z$ as the unit of length, this becomes

$$\left(\nabla^2 - \frac{1}{4} + \frac{n'}{r} - n'fz\right)\psi = 0,$$
$$f = \left(\frac{n'a_H}{2Z}\right)^2 \cdot \frac{F}{Ze}. \tag{41.27a}$$

Here f is the field strength measured in multiples of the field strength from the nuclear charge Ze at a distance equal to the new unit of length $n'a_H/2Z$. Multiplying by r, we obtain from (41.27*a*)

$$[(\xi + \eta)\nabla^2 - \tfrac{1}{4}(\xi + \eta) + \eta' - n'f(\xi^2 - \eta^2)]\psi = 0. \tag{41.28}$$

This equation is separable in ξ and η. Writing

$$\psi = X(\xi)Y(\eta)e^{im\varphi},$$
$$n' = \kappa_1 + \kappa_2 + 1, \tag{41.28a}$$

we find by means of (41.25) the equations

$$\left(\frac{d}{d\xi}\xi\frac{d}{d\xi} - \frac{m^2}{4\xi} - \frac{\xi}{4} + \kappa_1 + \frac{m+1}{2} - n'f\xi^2\right)X = 0,$$
$$\left(\frac{d}{d\eta}\eta\frac{d}{\partial\eta} - \frac{m^2}{4\eta} - \frac{\eta}{4} + \kappa_2 + \frac{m+1}{2} + n'f\eta^2\right)Y = 0. \tag{41.28b}$$

For $f = 0$, κ_1 and κ_2 must be integers k_1, $k_2 = 0, 1, 2, \cdots$; (41.28*b*) are then the well-known equations for the Laguerre functions

$$X_{km}(\xi) = \text{konst } e^{-\frac{1}{2}\xi}\xi^{\frac{1}{2}}L^m_{m+k}(\xi)$$

By (41.27) and (41.28*a*) the unperturbed energy is then

$$E_{k_1k_2m} = -\frac{Z^2Rh}{n^2}, \qquad n = k_1 + k_2 + m + 1. \tag{41.29}$$

For $f \neq 0$, we may calculate first-order perturbations of κ_1 and κ_2 by the method described above, and hence find the perturbed energy. Let us assume that the constant in $X_{km}(\xi)$ is chosen such that

$$\int_0^\infty [X_{km}(\xi)]^2\, d\xi = 1.$$

We have then as a first approximation that

$$\begin{aligned} \kappa_1 &= k_1 + nf\int_0^\infty [X_{k_1m}(\xi)]^2\xi^2\, d\xi, \\ \kappa_2 &= k_2 - nf\int_0^\infty [X_{k_2m}(\xi)]^2\xi^2\, d\xi. \end{aligned} \tag{41.30}$$

The calculation of these integrals will be left for the exercises; we only state the result

$$\int_0^\infty [X_{km}(\xi)]^2\xi^2\, d\xi = 6k^2 + 6k(m+1) + (m+1)(m+2). \tag{41.31}$$

This yields

$$n' = \kappa_1 + \kappa_2 + m + 1 = n(1 + 6(k_1 - k_2)nf). \tag{41.32}$$

By expanding $1/n'^2$ in (41.27) in powers of f we then obtain from (41.32) the first-order perturbation energy

$$E' = \frac{Z^2Rh}{n^2} \cdot 12(k_1 - k_2)nf. \tag{41.33}$$

If we wish to express the perturbation E' directly in terms of the field, we must substitute the last equation (41.27*a*) for f; substituting the values of Rh and a_H at the same time, we then find

$$E' = \frac{3h^2}{8\pi^2 m_0 Ze}(k_1 - k_2)nF. \tag{41.34}$$

We see that the effect is proportional to F and n, and inversely proportional to Z. These properties are easily visualized by our picture of the atom:

a large n, for instance, signifies a weaker binding of the electron. Finally we note that the number $k_1 - k_2$ is a measure of the asymmetry of the wave function in the z-direction; a large k_1 signifies that the statistical electronic charge is "stretched" along the positive direction of the z-axis, and conversely for large values of k_2.

Problems

1. The differential equation for the Laguerre polynomial is

$$\left[x\frac{d^2}{dx^2} + (1-x)\frac{d}{dx} + n\right]L_n(x) = 0.$$

Show that the equation for the mth derivative of $L_{n+m}(x)$ is

$$\left[x\frac{d^2}{dx^2} + (m+1-x)\frac{d}{dx} + n\right]L^m_{n+m}(x) = 0.$$

2. Show that the differential equation for $y_{nm} = e^{-(x/2)}x^{(m/2)}L^m_{n+m}(x)/(n+m)!$ is

$$\left(x\frac{d^2}{dx^2} + \frac{d}{dx} - \frac{m^2}{4x} - \frac{x}{4} + n + \frac{m+1}{2}\right)y_{nm}(x) = 0.$$

3. We have

$$\frac{\exp\left(\dfrac{-xs}{1-s}\right)}{1-s} = \sum_{n=0}^{\infty}\frac{L_n(x)}{n!}s^n.$$

Show that

$$\frac{\exp\left(\dfrac{-xs}{1-s}\right)}{(1-s)^{m+1}} = (-1)^m\sum_{n=0}^{\infty}\frac{L^m_{n+m}(x)}{(n+m)!}s^n,$$

and that

$$\Psi_m(x,s) = \frac{\exp\left(-\dfrac{x}{2}\cdot\dfrac{1+s}{1-s}\right)}{(1-s)^{m+1}}x^{(m/2)} = \sum_{n=0}^{\infty}y_{nm}(x)s^n.$$

4. Show, by multiplication by $\Psi_m(x,s)$ and $\Psi_m(x,t)$, and subsequent integration that

$$\int_0^\infty [y_{nm}(x)]^2\,dx = \frac{(n+m)!}{n!}, \quad \int_0^\infty [y_{nm}(x)]^2 x\,dx = \frac{(n+m)!}{n!}(2n+1+m),$$

$$\int_0^\infty [y_{nm}(x)]^2 x^2\,dx = \frac{(n+m)!}{n!}[6n^2 + 6n(m+1) + (m+1)(m+2)].$$

Use this to verify (41.31).

5. Consider (41.27*a*). Write $n' = n + 2$ in the unperturbed equation and show that

$$\psi_1 = e^{-(r/2)}(2 - r)$$

and

$$\psi_2 = e^{-(r/2)}z$$

are solutions of this equation. Show, using ordinary perturbation methods, that we obtain

$$n = 2 \pm 24f$$

as a first approximation. Show that the corresponding functions are

$$\psi_1 - \psi_2 = e^{-(r/2)}(2 - (r + z)) = 2e^{-\frac{1}{2}(\xi+\eta)}(1 - \xi)$$

and

$$\psi_1 + \psi_2 = 2e^{-\frac{1}{2}(\xi+\eta)}(1 - \eta)$$

and that this corresponds to the cases $k_1 = 1$, $k_2 = 0$ and $k_1 = 0$, $k_2 = 1$. Finally show that

$$n' = 2 \pm 24f$$

agrees with (41.31).

42. TIME-DEPENDENT PERTURBATIONS

Change of a System by Time-Dependent Forces

If the Hamiltonian for a system is explicitly dependent on time, $H = H(q, p, t)$, the system will no longer possess stationary states. In this case we must treat the system and its changes of state by means of the general time-dependent wave equation

$$Hu = -\frac{h}{2\pi i}\frac{\partial u}{\partial t}. \tag{42.1}$$

As a rule it will be possible to separate out the time-dependent terms of the Hamiltonian; these may then be denoted by $H'(q, p, t)$ and regarded as perturbations. The time average of such perturbations will often vanish, for example, for periodic disturbances; however, we shall assume that it may also be different from zero in order not to specialize the argument too much. In any case we shall put

$$H = H^\circ(q, p) + H'(q, p, t), \tag{42.2}$$

where H° is time-independent and thus possesses stationary states

$$\begin{gathered} u_n = \psi_n \exp\left[-\left(\frac{2\pi i}{h}\right)E_n t\right] \\ H^\circ u_n = -\frac{h}{2\pi i}\frac{\partial u_n}{\partial t}, \\ H^\circ \psi_n = E_n \psi_n, \\ \int u_m^* u_n \, d\tau = \int \psi_m^* \psi_n \, d\tau = \delta_{mn}. \end{gathered} \tag{42.3}$$

The natural procedure is now to try to describe the system and its changes of state by means of these eigenstates and functions. This may be done by writing

$$u = \sum_n c_n(t)u_n, \tag{42.4}$$

where the expansion coefficients are no longer constants, but time-dependent functions. Substitution in (42.1 yields)

$$\sum_n \left(c_n H' + \frac{h}{2\pi i}\dot{c}_n\right)u_n = 0. \tag{42.5}$$

We now take advantage of the fact that the functions u_n or ψ_n constitute a complete orthonormal set. Multiplying (42.5) by u_n^* and integrating over the entire coordinate space of our system, we obtain

$$\frac{h}{2\pi i}\dot{c}_m + \sum_n H'_{mn}e^{i\omega_{mn}t}c_n = 0. \tag{42.6}$$

and

$$\begin{aligned} H'_{mn} &= \int \psi_m^* H' \psi_n \, d\tau, \\ \omega_{mn} &= \frac{2\pi}{h}(E_m - E_n) = 2\pi\nu_{mn}. \end{aligned} \tag{42.6a}$$

This is a set of simultaneous differential equations for the coefficients c_n; these are normalized, together with u in (42.4), by the condition

$$\int u^* u \, d\tau = \sum_n c_n^* c_n = 1. \tag{42.7}$$

It is easily seen by means of (42.1) and the corresponding equation for u^*,

$$Hu^* = \frac{h}{2\pi i}\frac{\partial u^*}{\partial t}\,[1] \tag{42.7a}$$

that (42.7) is valid for all t-values if it is valid for one. For we must have

$$\frac{h}{2\pi i}\frac{\partial}{\partial t}\int u^* u \, d\tau = \int (uHu^* - u^* Hu)\, d\tau = 0, \tag{42.7b}$$

since H is taken to be self-adjoint.

[1] When using the complex conjugate wave function u^*, we shall assume that the ordinary momentum and energy operators change as follows:

$$p \to -\frac{h}{2\pi i}\frac{\partial}{\partial q}, \qquad E \to \frac{h}{2\pi i}\frac{\partial}{\partial t}.$$

In general this may be written as

$$Fu^* = (Fu)^*.$$

The simultaneous set (42.6) is not solvable in general, and we must be content with approximate solutions. The physical situation is often such that we may assume that the system is in a given state $u = u_n$ at a time $t = 0$, so that $c_n(0) = 1$ and $c_m(0) = 0$ for $m \neq n$. The problem is then to determine the values of the coefficients at a later time t, that is, to find how rapidly the system passes from the state u_n to the other states u_m.

For not too large time intervals, where the coefficients are still small and c_n thus practically equal to unity, we obtain from (42.5) as a first approximation,

$$c_m = -\frac{2\pi i}{h}\int_0^t H'_{mn}e^{i\omega_{mn}t}\,dt. \tag{42.8}$$

The coefficients c_m themselves have no direct physical significance; but the quantity $|c_m|^2 = c_m^* c_m$ represents by (42.7) the weight of the state u_m in the composite state u, that is, the probability of finding the system in the state u_m at the time t. If $|c_m|^2$ increases uniformly with t, we may speak of a time-independent transition probability; this which may be defined as

$$\frac{d}{dt}|c_m|^2 = \frac{1}{t}|c_m|^2, \tag{42.9}$$

then represents the probability of the quantum transition $n \rightarrow m$ taken per unit time.

Periodic Perturbations

If the perturbation of an atom is periodic in time, for example, an incident electromagnetic wave, we may put

$$H' = Fe^{-i\omega t} + \bar{F}e^{i\omega t}, \tag{42.10}$$

where F and $\bar{F}$ are *complex conjugate* or *adjoint operators*.[1] For these we have, in general,

$$\bar{F}^*_{mn} = \int \psi_n^* F \psi_m \, d\tau = F_{nm}. \tag{42.11}$$

By means of (42.8) we thus obtain

$$c_m = \frac{2\pi}{h}\left[F_{mn}\frac{1 - e^{i(\omega_{mn}-\omega)t}}{\omega_{mn} - \omega} + F^*_{nm}\frac{1 - e^{i(\omega_{mn}+\omega)t}}{\omega_{mn} + \omega}\right]. \tag{42.12}$$

It follows that c_m will in general (that is, for arbitrary ω) have an oscillatory character and not increase uniformly with time. If, however, ω coincides with the combination frequency $|\omega_{mn}|$ for the transition $n \rightarrow m$, a kind of resonance will occur, and c_m will increase linearly with t. Nevertheless

[1] $x + iy$ and $M_x + iM_y$ are complex operators, and their adjoints are $x - iy$ and $M_x - iM_y$. On the other hand, $p_x = \frac{h}{2\pi i}\frac{\partial}{\partial x}$ is a *real* or *self-adjoint* operator, $\bar{p}_x = p_x$.

since $|c_m|^2$ will then be proportional to t^2, our condition for a unique definition of the transition probability breaks down.

However, electromagnetic radiation (or, in general, any perturbing force) is never strictly monochromatic. We must therefore take $|F_{mn}|^2$ to be a function of the variable frequency ω and integrate $|c_m|^2$ over a small frequency interval around the resonance point $\omega = |\omega_{mn}|$. It is then the first or last term that contributes to the transition probability, according as ω_{mn} is positive or $\omega_{mn} = -\omega_{nm}$ is negative. Hence F_{mn} and F^*_{nm} are the matrix element for absorption and emission, respectively. Thus we only have to consider one of the terms in (42.12), for example, the first (for $E_m > E_n$). We then find that

$$|c_m|^2 \approx \left(\frac{2\pi}{h}\right)^2 |F_{mn}|^2 \frac{2(1 - \cos(\omega_{mn} - \omega)t)}{(\omega_{mn} - \omega)^2}. \tag{42.13}$$

This quantity is dimensionless; hence we must, when integrating over ω, multiply by a quantity $\rho(\nu)$ with the dimension reciprocal frequency or time. We write the relative distribution of the perturbation in the frequency interval considered as

$$\rho(\nu)\, d\nu = \frac{1}{2\pi} \rho(\nu)\, d\omega, \tag{42.14}$$

and introduce

$$x = (\omega - \omega_{mn})t \tag{42.15}$$

as a new variable with limits $x = \pm\infty$ for sufficiently large t. Since

$$\int_{-\infty}^{+\infty} \frac{1 - \cos x}{x^2}\, dx = \pi, \tag{42.15a}$$

we then obtain

$$|c_m|^2 = \left(\frac{2\pi}{h}\right)^2 |F_{mn}|^2\, \rho(\nu_{mn})t. \tag{42.16}$$

Hence the transition probability for absorption is

$$\frac{1}{t}|c_m|^2 = \left(\frac{2\pi}{h}\right)^2 |F_{mn}|^2\, \rho(\nu_{mn}). \tag{42.16a}$$

For emission a completely analogous formula is easily found by exchanging ν_{mn} and F_{mn} with ν_{nm} and F_{nm}.

Absorption and Emission in a Radiation Field

Let us consider a plane electromagnetic wave propagating in the direction $\mathbf{n}$, and with the polarization direction $\mathbf{e}$,

$$\mathbf{E} = \mathbf{e}E(\omega) \sin \omega\left(t - \frac{\mathbf{nr}}{c}\right), \qquad \mathbf{H} = \mathbf{n} \times \mathbf{E}, \tag{42.17}$$

$$div\, \mathbf{E} = 0, \qquad \mathbf{ne} = 0, \qquad \mathbf{n}^2 = 1, \qquad \mathbf{e}^2 = 1.$$

This field is derivable from a divergence-free vector potential **A**,

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, \qquad \mathbf{H} = \operatorname{curl} \mathbf{A}, \qquad \operatorname{div} \mathbf{A} = 0. \tag{42.18}$$

For this potential we find the following expression

$$\mathbf{A} = \frac{c}{\omega}\,\mathbf{e}E(\omega)\cos\omega\left(t - \frac{\mathbf{nr}}{c}\right) = \frac{c}{2\omega}\,\mathbf{e}E(\omega)(e^{ik\mathbf{nr}-i\omega t} + e^{-ik\mathbf{nr}+i\omega t}). \tag{42.19}$$

$$k = \frac{\omega}{c} = \frac{2\pi}{\lambda}.$$

Utilizing the fact that the potential **A** is divergence-free, we write the perturbation energy as

$$H' = \frac{1}{2m_0}\left[\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\right)^2 - \mathbf{p}^2\right] = \frac{e}{m_0 c}\,\mathbf{Ap} + \frac{e^2}{m_0 c^2}\,\mathbf{A}^2, \tag{42.20}$$

or more briefly as

$$H' = \frac{e}{m_0 c}\,\mathbf{Ap}, \tag{42.20a}$$

assuming, for the moment, that the last term is insignificant and may be neglected. By means of (42.19) we then obtain the perturbation energy

$$H' = Fe^{-i\omega t} + \bar{F}e^{i\omega t},$$

$$F = \frac{eE(\omega)}{2m_0\omega}\,e^{ik\mathbf{nr}}p_e, \tag{42.21}$$

where p_e denotes the component of momentum in the direction of polarization.

If the radiation frequency ω is to be close to the eigenfrequency ω_{mn} of the atom, λ must be very large relative to the atomic dimensions and k correspondingly small, so that we may—without any noticeable error—put $e^{ik\mathbf{nr}} = 1$. Then F is a self-adjoint operator, and we find

$$F_{mn} = \frac{eE(\omega)}{2m_0\omega}(p_e)_{mn} = \frac{i\omega_{mn}}{2\omega}\,eE(\omega)(x_e)_{mn}, \tag{42.22}$$

since it may be shown that, in general,

$$(p_w)_{mn} = i\omega_{mn}m_0 x_m. \tag{42.22a}$$

A comparison with (42.17) shows that essentially the same result would have been obtained by using the expression $H' = e\mathbf{rE}$ for the perturbation energy. More precisely, we should have gotten the same result as in (42.22)

apart from the factor ω_{mn}/ω. However, this factor will disappear in the calculation of absorption or emission, since then only the frequency region around $\omega = \omega_{mn}$ contributes to the integral.

In the expression for $|F_{mn}|^2$ there now appears a factor $E^2(\omega)$ which may be expressed in terms of the mean energy density u as follows

$$E^2(\omega) = 8\pi u. \tag{42.23}$$

When calculating the time average of the energy, a factor $\frac{1}{2}$ will appear, since $\overline{\sin^2 \omega t} = \frac{1}{2}$; however, this is compensated by an equal magnetic energy. By the preceding considerations we should replace (42.23) by

$$E^2(\omega) = 8\pi \int u(\nu)\, d\nu, \tag{42.23a}$$

and thus also $\rho(\nu)$ in (42.14) by

$$\rho(\nu) = \frac{8\pi u(\nu)}{E^2(\omega)} \qquad \text{or} \qquad E^2(\omega)\rho(\nu) = 8\pi u(\nu). \tag{42.23b}$$

Utilizing (42.16*a*) and (42.22), we then find that the transition probability for absorption is given by

$$\frac{1}{t}|c_m|^2 = \frac{8\pi^3}{h^2} e^2 u(\nu_{mn})\, |(x_e)_{mn}|^2. \tag{42.24}$$

Up to now we have considered unidirectional radiation only. For spatially isotropic radiation the density will be three times as large, so that $u(\nu)$ must be replaced by $\frac{1}{3}u(\nu)$. At the same time the square of the matrix elements for all the three principal directions of polarization must be included; hence we obtain as a final result:

$$\frac{1}{t}|c_m|^2 = \frac{8\pi^3}{3h^2} e^2 u(\nu_{mn})\, |\mathbf{r}_{mn}|^2. \tag{42.25}$$

For emission exactly the same formula results, whence follow the values of the Einstein coefficients for absorption and *induced* emission

$$B_{nm} = B_{mn} = \frac{8\pi^3 e^2}{3h^2} |\mathbf{r}_{mn}|^2. \tag{42.26}$$

Concerning the coefficient A_{mn} for spontaneous emission we must at present content ourselves with the considerations previously carried out in the discussion of Einstein's deduction of Planck's law of radiation. By (7.5) A_{mn} may be obtained from B_{mn} by multiplying with $8\pi\nu^2 \cdot h\nu/c^3$; hence the coefficient of spontaneous emission

$$A_{mn} = \frac{64\pi^4 \nu^3 e^2}{3c^3 h} |\mathbf{r}_{mn}|^2, \tag{42.27}$$

The spontaneously emitted energy per unit time is

$$\bar{\eta}_{mn} = h\nu A_{mn} = \frac{64\pi^4\nu^4 e^2}{3c^3} |\mathbf{r}_{mn}|^2, \tag{42.28}$$

in agreement with previous formulas. Since h has disappeared from (42.28), this expression may be compared with the radiation from a classical oscillator. Writing (42.28) as

$$\bar{\eta}_{mn} = \frac{\omega^4 e^2}{3c^3} |2\mathbf{r}_{mn}|^2, \tag{42.28a}$$

it is evident that the radiation corresponds to that of a classical oscillator with the amplitude $|2\mathbf{r}_{mn}|$.

Problems

1. Show that the perturbation function for an atom with an arbitrary number of electrons e_i in a radiation field may be written

$$H' = \frac{e}{m_0 c} \sum_i \mathbf{A}_i \mathbf{p}_i + \frac{e^2}{2m_0 c^2} \sum_i \mathbf{A}_i^2.$$

2. Show, by means of the wave equation

$$\left(\frac{1}{2m_0} \mathbf{p}^2 + V\right) \psi_n = E_n \psi_n$$

for a single electron and the corresponding equation for ψ_m^*, that

$$(p_x)_{mn} = 2\pi i \nu_{mn} m_0 x_{mn} = i\omega_{mn} m_0 x_{mn}.$$

(Hint: Multiply the equations by $x\psi_m^*$ and $x\psi_n$, subtract and integrate, making use of the commutator for x and p_x.)

3. Show that the same equation is valid for the coordinate and momentum matrices of an atom with several electrons,

$$\mathbf{r} = \sum_i \mathbf{r}_i, \quad \mathbf{p} = \sum_i \mathbf{p}_i.$$

4. Show, by integrating in parts, that

$$I = \int_{-\infty}^{+\infty} \frac{1 - \cos x}{x^2} dx = \int_{-\infty}^{+\infty} \frac{\sin x}{x} dx.$$

Calculate this integral in the following way: Put

$$\frac{1}{x} = \int_0^\infty e^{-\alpha x} d\alpha$$

and determine the resulting double integral by interchanging the order of integrations.

43. DISPERSION THEORY

The Electric Dipole Moment of an Atom in a Radiation Field

For simplicity we consider an atom with only one electron. When this electron is in a point $\mathbf{r}$, it will exhibit—together with a compensating charge in the atomic nucleus—a dipole moment $-e\mathbf{r}$. Since $|u|^2$ denotes the mean statistical electron distribution, the atom will (as a whole) have a mean dipole moment

$$\mathbf{P} = -e\int u^* r u \, d\tau. \tag{43.1}$$

As long as the atom is in a single stationary state u_n, that is, $c_n = 1$, $c_m = 0$, $m \neq n$, the dipole moment will be zero. However, if it passes over into a composite state, say $u = c_n u_n + c_m u_m$, under the influence of perturbing forces, it will have the dipole moment

$$\mathbf{P}_{mn} = -e(c_m^* c_n \mathbf{r}_{mn} e^{i\omega_{mn}t} + c_n^* c_m \mathbf{r}_{nm} e^{-i\omega_{mn}t}). \tag{43.2}$$

the magnitude of which depends on c_n and c_m. Starting with the state u_n at $t = 0$ and considering a perturbation of the form (42.10), we may then take c_n to be approximately unity while c_m is given by (42.12).

Furthermore we assume that the perturbation is due to an electromagnetic wave of the form (42.17), moving in the z-direction with a polarization directed along the x-axis. It is easily seen that $\mathbf{P}_{mn}$ will then only have a component in the x-direction. Summing over all states m, we find

$$P_x = -e\sum_m (c_m^* x_{mn} e^{i\omega_{mn}t} + c_m x_{nm} e^{-i\omega_{mn}t}). \tag{43.3}$$

As before, we assume that the wavelength of the incident radiation is large so that the exponential function $e^{ik\mathbf{nr}} = e^{ikz}$ may be omitted in (42.21); we may then write as in (42.22),

$$\begin{aligned} \bar{F} = F &= \frac{eE(\omega)}{2m_0\omega} p_x, \\ F_{mn} &= \frac{i\omega_{mn}}{2\omega} eE(\omega) x_{mn}. \end{aligned} \tag{43.4}$$

By means of (42.13) we then obtain (with $F_{mn}^* = F_{mn}$)

$$P_x = \sum_m{}' \frac{\pi\omega_{mn}}{ih\omega} e^2 E(\omega) |x_{mn}|^2 \cdot \left(\frac{e^{-i\omega_{mn}t} - e^{-i\omega t}}{\omega_{mn} - \omega} + \frac{e^{-i\omega_{mn}t} - e^{i\omega t}}{\omega_{mn} + \omega} - \frac{e^{i\omega_{mn}t} - e^{i\omega t}}{\omega_{mn} - \omega} - \frac{e^{i\omega_{mn}t} - e^{-i\omega t}}{\omega_{mn} + \omega} \right). \tag{43.5}$$

Here several terms appear, representing partly free oscillations with the proper frequencies ω_{mn} of the atom, partly forced oscillations with the externally imposed frequency ω. It is the latter that are of primary interest here; the former die rapidly away because of the radiation damping, just as the free oscillations of a classical damped oscillator. Actually the problem of how these transient oscillations are touched off and die away has already been solved in our discussion of absorption and emission. Thus we omit these phenomena in (43.5) which leaves us with

$$P_x = \sum_m{}' \frac{2\pi\omega_{mn}}{h\omega} e^2 E(\omega) |x_{mn}|^2 \sin \omega t \left(\frac{1}{\omega_{mn} - \omega} - \frac{1}{\omega_{mn} + \omega} \right)$$

$$= \frac{4\pi e^2}{h} E(\omega) \sin \omega t \cdot \sum_m{}' \frac{\omega_{mn} |x_{mn}|^2}{\omega_{mn}{}^2 - \omega^2}. \tag{43.6}$$

This result is very instructive. By (42.17) the quantity $E(\omega) \sin \omega t$ is, for large wavelengths, equal to the magnitude of the electric vector. For a single classical oscillator we should have the following ratio between the polarization vector and the electric vector

$$\frac{P}{E} = \frac{e^2}{m_0(\omega_0{}^2 - \omega^2)}, \tag{43.7}$$

where ω_0 is the proper frequency of the oscillator, and m_0 the mass of the oscillating particle. From (43.6), however, we obtain

$$\frac{P}{E} = \sum_m{}' \frac{e^2 f_{mn}}{m_0(\omega_{mn}{}^2 - \omega^2)}, \tag{43.8}$$

where

$$f_{mn} = \frac{4\pi}{h} m \omega_{mn} |x_{mn}|^2 = \frac{4\pi i}{h} p_{xnm} x_{mn} = \frac{2\pi i}{h} (p_{xnm} x_{mn} - x_{nm} p_{xmn}). \tag{43.9}$$

Hence the classical oscillator is here distributed, as it were, among several oscillators of different frequencies; these oscillators then have the fractions f_{mn}, known as the oscillator strengths, of the "classical strength." For these oscillator strengths we have an interesting relation, known as the Thomas-Kuhn sum rule, namely,

$$\sum_m f_{mn} = 1. \tag{43.10}$$

This follows immediately from (43.9); by the rules of matrix multiplication we find that

$$\sum_m{}' f_{mn} = \frac{2\pi i}{h} (p_x x - x p_x)_{nn} = \frac{2\pi i}{h} \cdot \frac{h}{2\pi i} = 1. \tag{43.10a}$$

For atoms with Z electrons it may be shown that a summation over all states u_m (which represent a possible dipole transition from u_n) yields

$$\sum_m{}' f_{mn} = Z. \tag{43.11}$$

Refraction and Dispersion

By classical electromagnetic theory the propagation velocity of light waves is $v = c/n$, where $n = \sqrt{\varepsilon\mu}$ is the index of refraction. For many substances $\mu \approx 1$, so that $n^2 = \varepsilon$; since $D = \varepsilon E$, we then obtain

$$n^2 = \varepsilon = \frac{D}{E} = 1 + 4\pi\frac{P}{E}. \tag{43.12}$$

In this formula E is the mean electric field, while E in (43.8) is the field acting on the atomic electrons; as shown in Part III, on electromagnetism, the latter field is actually equal to $E + (4\pi/3)P$ if E is the mean field. Hence we must replace E by $E + (4\pi/3)P$ in (43.8) and also multiply by the number of atoms N per unit volume. It is then convenient to rewrite (43.12) as

$$\frac{n^2 - 1}{n^2 + 2} = \frac{(4\pi/3)P}{E + (4\pi/3)P} = \sum_m{}' \frac{4\pi N e^2 f_{mn}}{3m_0(\omega_{mn}{}^2 - \omega^2)}. \tag{43.13}$$

This is the classical *dispersion relation* for the index of refraction for undamped electric oscillators; the later are here, however, characterized by the quantum-mechanical proper frequencies ω_{mn} and the corresponding oscillator strengths f_{mn}, of the atom.

The phenomena accompanying resonances, that is, $\omega = \omega_{mn}$, are usually referred to as *anomalous refraction* and *anomalous dispersion;* in order to describe them correctly it is necessary to take into account the radiation damping.

Scattering of Long-Wave Electromagnetic Radiation

Using the classical expressions for radiation from a dipole, we may calculate the radiation due to the forced oscillations in the atom; this radiation will be regarded as a scattering of the incident radiation.

If the atom has an oscillating electric dipole moment with the frequency ω, the electric vector for the emitted radiation in the wave zone will be

$$E' = \frac{\omega^2 P}{rc^3}\sin\Theta, \tag{43.14}$$

where Θ is the angle between the polarization vector and the ray direction. If E is the electric vector for the incident radiation we find

$$\frac{E'}{E} = \frac{\omega^2}{rc^2}\cdot\frac{P}{E}\sin\Theta. \tag{43.15}$$

The ratio between the incident radiation per unit area and scattered radiation per unit solid angle will be referred to as the differential scattering cross section, and denoted by $\sigma(\vartheta)$; it may be defined as $\sigma(\vartheta) = r^2(E'/E)^2$.

If the scattered radiation is in the same plane as E and P, we shall have $\sin\Theta = \cos\vartheta$; and if it is in a plane perpendicular to E and P, we have $\sin\Theta = 1$. This yields for the mean intensity of scattered radiation the so-called Thomas factor $\frac{1}{2}(1 + \cos^2\vartheta)$ for unpolarized radiation. Using (43.15) and (43.8), we thus find a differential scattering cross section for coherent long-wave radiation

$$\sigma(\vartheta) = \frac{1 + \cos^2\vartheta}{2} r_0^2 f^2,$$
$$r_0 = \frac{e^2}{m_0 c^2}, \qquad f = \sum_m{}' \frac{\omega^2 f_{mn}}{\omega_{mn}^2 - \omega^2}, \tag{43.16}$$

where r_0 has the dimension of length and corresponds to the classical or Thomson electron radius. Here f is a dimensionless quantity which corresponds to the so-called atomic form factors. We shall meet these later, when we consider scattering problems in more detail: however, we note at this stage that the "long-wave" f in (43.16) does not depend on the scattering angle ϑ, as do the atomic form factors for short-wave scattering.

Problems

1. Show, by means of the transition $\omega \to \infty$ or $\omega_{mn} \to 0$ and using the sum rule for f_{mn}, that (43.16) gradually reduces to the scattering formula for free electrons, with the total scattering cross section
$$\sigma = \frac{8\pi}{3} r_0^2.$$

2. Show, using the methods of matrix analysis, that
$$\sum_m{}' |r_{mn}|^2 = \int \psi_n^* r^2 \psi_n \, d\tau.$$

3. Show directly, using the wave equation, that we have
$$\sum_m{}' f_{mn} = 1$$
for an atom with only one electron; and also, by an analogous definition of f_{mn} for an atom with Z electrons, that we have
$$\sum_m{}' f_{mn} = Z$$
in this case.

CHAPTER 7

The Quantum Theory of Many-Electron Systems

44. SYSTEMS OF IDENTICAL PARTICLES

Wave Functions and Symmetry

Several fundamental aspects of quantum mechanics appear only in the treatment of atoms or molecules with more than one electron. Chemical binding forces, for instance, may be understood as arising from a specific relation between two electrons constituting an electron pair. Here, however, we shall content ourselves with the consideration of the following many-electron problem: a model atom with the nuclear charge Ze and N orbital electrons. According as $N \gtreqless Z$ this corresponds to a negative ion (which rarely appears in reality), a neutral atom (which is the case usually occurring), and a positive ion (which may always, in principle, be produced by experimental means). For simplicity we shall refer to them all as many-electron atoms.

The Hamiltonian of such an atom is

$$H = T + V + V', \tag{44.1}$$

where

$$T = \sum_{k=1}^{N} \frac{1}{2m_0} \mathbf{p}_k^2, \tag{44.2}$$

$$V = -\sum_{i=1}^{N} \frac{Ze^2}{r_i}, \tag{44.3}$$

$$V' = \sum_{i>k=1}^{N} \frac{e^2}{r_{ik}}, \tag{44.4}$$

here r_i is the distance between an electron and the nucleus, and r_{ik} the mutual distance between two electrons.

We note that the Hamiltonian is symmetric in the coordinates of all the electrons. This means that if we have obtained a solution of the energy equation

$$H\psi = E\psi, \tag{44.5}$$

then

$$\psi' = P_{ik}\psi \tag{44.6}$$

is also a solution of (44.5) with the same E. The so-called permutation operator P_{ik} denotes an interchange of the electron coordinates i and k; it commutes with H, as already found (compare Section 41) and has the eigenvalues

$$P_{ik} = \pm 1, \tag{44.7}$$

since $P_{ik}^2 = 1$. However, it is not possible to quantize all permutation operators simultaneously, since they are not mutually commutative. Thus we have, for instance,

$$P_{12}P_{23}\psi(1, 2, 3) = \psi(3, 1, 2) \tag{44.8}$$

but

$$P_{23}P_{12}\psi(1, 2, 3) = \psi(2, 3, 1). \tag{44.9}$$

The first product operator yields a cyclic, and the second an anticyclic, permutation. It is possible to quantize all permutation operators simultaneously only when they all have the eigenvalue $+1$ or the eigenvalue -1. The former leads to an eigenfunction that is symmetric in all coordinates,

$$\psi_s = \psi(\overline{1, 2, \cdots, N}), \tag{44.10}$$

the latter to a correspondingly antisymmetric eigenfunction.

$$\psi_a = \psi(\overbrace{1, 2, \cdots, N}). \tag{44.11}$$

The Pauli Principle

This principle says that two or more electrons in an N-electron system cannot be in the same quantum state. As an approximation to the wavefunction, we may try to write it as a product of one-electron functions, that is, a so-called Hartree product,

$$\psi = \psi_{n_1}(1)\psi_{n_2}(2) \cdots \psi_{n_N}(N). \tag{44.12}$$

It is then evident that the Pauli principle is equivalent to requiring that the wave function be antisymmetric, that is, expressible by means of a so-called Slater determinant,

$$\psi_a = \begin{vmatrix} \psi_{n_1}(1) & \psi_{n_1}(2) & \cdots & \psi_{n_1}(N) \\ \psi_{n_2}(1) & \psi_{n_2}(2) & \cdots & \psi_{n_2}(N) \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \end{vmatrix}. \tag{44.13}$$

Here n_i represents not only one, but a complete set of quantum numbers for a single electron. As soon as two of these coincide, $n_i = n_k$, the determinant becomes zero.

This would now indicate that we should use only antisymmetric wave functions to describe our N-electron problem. However, it is not quite as simple as that, since we must also quantize the electron spins in the one-electron functions in the usual way

$$\sigma_z = \pm 1, \qquad \text{or} \qquad s_z = \pm \tfrac{1}{2}\hbar. \tag{44.14}$$

If two electrons have opposite spins, that is, may be described by the spin function

$$A(1, 2) = \begin{vmatrix} \alpha(1) & \alpha(2) \\ \beta(1) & \beta(2) \end{vmatrix}, \tag{44.15}$$

the corresponding spatial wave function must be symmetric in the two electrons 1 and 2. These constitute a special electron pair which favors a symmetric wave function with a corresponding lower energy. The more such paired electrons occur, the more symmetric will be the wave function.

The other extreme would be the case where all electrons had equal spins corresponding, say, to

$$A(\overline{1, 2, \cdots, N}) = \alpha(1)\alpha(2) \cdots \alpha(N). \tag{44.16}$$

The spatial function would then assume the form of a Slater determinant as in (44.13). As an intermediate case we might have the first N_1 electrons with the same spin, and the remaining $N - N_1$ with the opposite spin,

$$A(\overline{1, 2, \cdots, N_1}, \overline{(N_1 + 1), \cdots, N}) = \alpha(1) \cdots \alpha(N_1)\beta(N_1 + 1) \cdots \beta(N). \tag{44.17}$$

The wave function may then be written as a product of two Slater determinants for the two types of electrons; however, this product must then be augmented by additional analogous products until the total wave function is antisymmetric in all the electrons. Nevertheless since each term of this total wave function satisfies the spatial wave equation, it is essential that the spatial wave function satisfy the condition

$$\psi = \psi(\overbrace{1, 2, \cdots, N_1}, \overbrace{N_1 + 1, \cdots, N}), \tag{44.18}$$

the electrons within each of the two groups are then taken to have, respectively, "positive" and "negative" spin directions.

In the case of the two-electron problem, which is the only one we shall consider here, the matter becomes very simple. We obtain the symmetric

and antisymmetric solutions

$$\psi_s = \psi(\overline{1, 2}), \qquad \psi_a = \psi(\widetilde{1, 2}). \tag{44.19}$$

This is the reason for the two different systems of emission and absorption lines in the helium spectrum. The two helium modifications have received the names *para-* and *ortho-helium* (corresponding to symmetric and antisymmetric wave functions). When helium was first discovered by spectral analysis of sunlight, it was natural to suspect that two different elements or atoms were involved. This was, of course, easily disproved when helium was isolated and purified in terrestrial laboratories.

45. METHODS OF APPROXIMATION

Perturbation Theory Treatment of the Helium Atom

We write, for the helium atom,

$$H = H^\circ + H', \tag{45.1}$$

where

$$H^\circ = -\frac{\hbar^2}{2m_0}(\nabla_1^2 + \nabla_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2}, \qquad H' = \frac{e^2}{r_{12}}.$$

The equation

$$H^\circ\psi^\circ = E^\circ\psi^\circ \tag{45.2}$$

is then easy to solve. The Hartree product

$$\psi^\circ = \psi_{n_1}(1)\psi_{n_2}(2) \tag{45.3}$$

is a solution if each separate function is a solution of the equation for the helium ion,

$$\left(\frac{\hbar^2}{2m_0}\nabla_i^2 + E + \frac{2e^2}{r_i}\right)\psi(i) = 0, \qquad i = 1, 2. \tag{45.4}$$

But (45.3) is also a solution if the coordinates are interchanged. The wave equation is thus degenerate and any linear combination is possible. However, as soon as we allow for the perturbation due to the interaction between the electrons, $H' = e^2/r_{12}$, two particular combinations are singled out:

$$\psi_{s,a} = 2^{-1/2}[\psi_{n_1}(1)\psi_{n_2}(2) \pm \psi_{n_1}(2)\psi_{n_2}(1)]. \tag{45.5}$$

The factor $2^{-1/2}$ has been added for purposes of normalization, since we have assumed that the separate functions appearing in (45.5) are normalized and mutually orthogonal.

We now obtain by means of the perturbation theory,

$$E = E^\circ + E', \tag{45.6}$$

$$E_s' = \int \frac{e^2}{r_{12}} \psi_s^{\,2}\, d\tau = I_1 + I_2, \tag{45.7}$$

$$E_a' = \int \frac{e^2}{r_{12}} \psi_a^{\,2}\, d\tau = I_1 - I_2, \tag{45.8}$$

and

$$I_1 = \int \frac{e^2}{r_{12}} \psi_{n_1}^{\,2}(1)\psi_{n_2}^{\,2}(2)\, d\tau, \quad I_2 = \int \frac{e^2}{r_{12}} \psi_{n_1}(1)\psi_{n_2}(1)\psi_{n_1}(2)\psi_{n_2}(2)\, d\tau. \tag{45.9}$$

The first integral I_1 describes the potential energy of two electrostatic charge distributions corresponding to the distributions $\psi_{n_1}^{\,2}(1)$, $\psi_{n_2}^{\,2}(2)$ of the two electrons. On the other hand, I_2 denotes the potential energy of two identical combination charges. Both integrals are positive. The most interesting one is I_2, the so-called exchange integral which has no classical analogue at all. By (45.7) and (45.8) the orthostates have the lowest energy, and the parastates the highest.

The particular case $n_1 = n_2$ yields only parastates,

$$\psi_s = \psi_n(1)\psi_n(2). \tag{45.10}$$

The ground state with $n = 1$ for the principal quantum numbers is of this type. It possesses the lowest energy of all states, since it has no competition from a corresponding orthostate. The remainder of the states (45.10) are usually of less interest, being doubly excited states. This also applies to the states (45.5), except the case when n_1 or n_2 represent the ground state for the helium ion.

For a one-electron atom the eigenfunctions are most conveniently expressed using the unit $a_H/2$ for length; this corresponds to putting $\hbar = 1$, $e = 1$, $m_0 = \frac{1}{2}$. The energy unit is then $4Rh$, since

$$Rh = \frac{m_0}{2}\left(\frac{e^2}{\hbar}\right)^2 \to \frac{1}{4}. \tag{45.11}$$

Since the Rydberg (Ry) is a more convenient unit for the energy parameter E, we may write

$$H_0 = -(\nabla_1^{\,2} + \nabla_2^{\,2}) - \frac{2}{r_1} - \frac{2}{r_2}, \qquad H' = \frac{1}{r_{12}}, \tag{45.12}$$

$$(H_0 + H')\psi = \frac{E}{4}\psi. \tag{45.13}$$

Another possibility is to take $a_H/2Z$ as the unit of length. Our wave equation may then be written

$$(H^\circ + H')\psi = \frac{E}{4}\psi,$$

$$H^\circ = -(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_1} - \frac{1}{r_2}, \qquad H' = \frac{1}{Zr_{12}}, \tag{45.14}$$

with $Z = 2$. The energy parameter is then measured in the unit Z^2 Ry, or 4 Ry for helium. The advantage of (45.14) is that $1/Z$ may now be used as a perturbation parameter.

The unperturbed wave equation yields

$$\psi^\circ = \frac{1}{8\pi} e^{-\frac{r_1+r_2}{2}}, \qquad E^\circ = -2. \tag{45.15}$$

The perturbation energy is

$$E' = \frac{4}{Z}\frac{1}{(8\pi)^2}\int \frac{e^{-r_1-r_2}}{r_{12}}\, d\tau. \tag{45.16}$$

We now utilize the well-known expansion

$$\frac{1}{r_{12}} = \sum_{l=0} \frac{r_1^{\,l}}{r_2^{l+1}} P_l(\cos\vartheta), \qquad r_2 > r_1, \tag{45.17}$$

where

$$\cos\vartheta = \cos\vartheta_1 \cos\vartheta_2 + \sin\vartheta_1 \sin\vartheta_2 \cos(\varphi_2 - \varphi_1); \tag{45.18}$$

actually we shall only need the first term.

By reasons of symmetry we may integrate over only the half-space $r_2 > r_1$ and multiply by two; this leads to

$$E' = \frac{2}{Z}\int_0^\infty dr_1\, e^{-r_1} r_1^{\,2} \int_r^\infty e^{-r_2} r_2\, dr_2 = \frac{2}{Z}\int_0^\infty e^{-2r}(r^3 + r^2)\, dr = \frac{5}{4}\frac{1}{Z}. \tag{45.19}$$

The energy then becomes, in Rydberg units,

$$E = -2Z^2 + \tfrac{5}{4}Z, \tag{45.20}$$

that is, an energy of ionization for the first electron equal to $Z^2 - \frac{5}{4}Z$, or

$$1.5 \text{ Ry} = 20.40 \text{ eV}, \qquad (\text{Ry} = 13.60 \text{ eV}) \tag{45.21}$$

which may be compared with the experimental result

$$1.807 \text{ Ry} = 24.58 \text{ eV}. \tag{45.22}$$

Improvement of the Unperturbed Function

The result may be considerably improved by including some of the unperturbed potential energy in the perturbation function, in such a way that the first-order perturbation energy vanishes. Let us write the wave equation as

$$\left(\nabla_1^2 + \nabla_2^2 + \frac{E}{4} + V - V'\right)\psi = 0,$$
$$V = \left(1 - \frac{5}{16}\frac{1}{Z}\right)\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \qquad V' = \frac{1}{Z}\left[\frac{1}{r_{12}} - \frac{5}{16}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\right] \tag{45.23}$$

and define

$$L = \int \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi^2 \, d\tau, \tag{45.24}$$

$$L' = \int \frac{1}{r_{12}}\psi^2 \, d\tau. \tag{45.25}$$

The substitution of the wave function (45.15) would then yield $L = 1$, $L' = \frac{5}{16}$, so that the perturbation integral vanishes. The same would result if we use the wave function

$$\psi = \frac{k^3}{8\pi} \exp\left[-\frac{1}{2}k(r_1 + r_2)\right], \tag{45.26}$$

moreover it is possible to choose k in such a way that (45.26) is the exact solution of the new unperturbed equation

$$\left[\nabla_1^2 + \nabla_2^2 + \frac{E^\circ}{4} + k\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\right]\psi = 0 \tag{45.27}$$

by putting

$$k = 1 - \frac{5}{16}\frac{1}{Z}. \tag{45.28}$$

It is easy to show that (45.26) satisfies (45.27). However, we now have an unperturbed energy differing from the previous one,

$$E^\circ = -2k^2 = -2\left(1 - \frac{5}{16}\frac{1}{Z}\right)^2 \tag{45.29}$$

or, in Rydberg units,

$$E = -2Z^2 + \tfrac{5}{4}Z - \tfrac{25}{128}. \tag{45.30}$$

The energy of ionization is thus increased by almost 0.2 Ry, or 2.7 eV; instead of (45.21), we obtain

$$1.7 \text{ Ry} = 23.1 \text{ eV} \tag{45.31}$$

which reduces the difference between the theoretically predicted and experimentally observed energy values to one-third, relative to (45.21).

Variational Theory Treatment to the First Order

If we choose an arbitrary wave function ψ, representing some more or less clearly defined state, the mean value of an operator F will then, according to well-known theory, be given by

$$\bar{F} = \frac{I}{N}, \qquad I = \int \psi^* F \psi \, d\tau, \qquad N = \int \psi^* \psi \, d\tau. \tag{45.32}$$

It is thus not absolutely necessary to normalize the wave equation.

We may now vary such a wave function in different ways, for example, by taking it to be a function of certain variational parameters as well. It may then happen that ψ comes very close to or even coincides with an eigenfunction for F. In the latter case we have

$$F\psi = F'\psi, \qquad \bar{F} = F'. \tag{45.33}$$

A necessary condition for this to occur is that $\delta I = 0$ under a constrained variation $\delta\psi$ of ψ such that $\delta N = 0$. Using the method of Lagrange multipliers, this may be written as

$$\delta I - F' \, \delta N = 0, \tag{45.34}$$

where the variation $\delta\psi$ is arbitrary (unconstrained) but with a subsequent determination of F'. The result is (45.33).

We now return to our helium problem, or two-electron problem, and introduce as a first variational parameter a dilation factor k. That is to say, we replace the coordinate vectors $\mathbf{r}$ with $\mathbf{r}' = k\mathbf{r}$, where k is variable. Omitting the dashes, we then obtain the two-electron equation

$$k^2(\nabla_1^2 + \nabla_2^2) + \left[\frac{E}{4} + k\left(\frac{1}{r_1} + \frac{1}{r_2}\right) - \frac{k}{Z}\frac{1}{r_{12}}\right]\psi = 0, \tag{45.35}$$

instead of (45.23). It follows from this that the mean value of the energy is

$$\frac{E}{4} N = -k\left(L - \frac{L'}{Z}\right) + k^2 M, \tag{45.36}$$

where

$$\begin{aligned} N &= \int \psi^2 \, d\tau, \qquad L = \int \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi^2 \, d\tau, \qquad L' = \int \frac{1}{r_{12}}\psi^2 \, d\tau, \\ M &= -\int \psi(\nabla_1^2 + \nabla_2^2)\psi \, d\tau = \int [(\nabla\psi_1)^2 + (\nabla\psi_2)^2] \, d\tau. \end{aligned} \tag{45.37}$$

In this coordinate system also we shall employ the wave equation (45.15),

$$\psi = \frac{1}{8\pi} \exp\left[-\frac{1}{2}(r_1 + r_2)\right] \tag{45.38}$$

which yields

$$N = 1, \qquad L = 1, \qquad L' = \tfrac{5}{16}, \qquad M = \tfrac{1}{2}. \tag{45.39}$$

By varying k we obtain the stationary value of E with respect to k, or

$$E = -\frac{(L - L'/Z)^2}{NM}. \tag{45.40}$$

This then leads to the same energy value as (45.29):

$$E = -2\left(1 - \frac{5}{16}\frac{1}{Z}\right)^2. \tag{45.41}$$

No matter what wave function is employed, a minimalization of the energy with respect to the dilation factor will yield

$$k = \frac{L - L'/Z}{2M}, \qquad k^2 M = \frac{1}{2} k\left(L - \frac{L'}{Z}\right); \tag{45.42}$$

in other words, the absolute value of the kinetic energy is always equal to half the potential energy. This is a special case of the so-called *virial theorem* which is valid in quantum mechanics as well as in classical mechanics.

Reduction to Three Independent Variables

In addition to the energy the total angular momentum

$$\mathbf{m} = \mathbf{m}_1 + \mathbf{m}_2, \qquad \mathbf{m}_i = \mathbf{r}_i \times \mathbf{p}_i \tag{45.43}$$

of the two-electron atom is also a constant of the motion.

As is well-known, the operator $\mathbf{m}$ for a single electron yields zero when applied to r. Hence it follows that $\mathbf{m}$ for a two-electron system will yield zero when applied to functions of r_1 and r_2. This will also be the case for r_{12} or for functions of the three variables r_1, r_2, and r_{12}, since, for example,

$$m_z r_{12} = \frac{i\hbar}{r_{12}} [x_1(y_1 - y_2) - y_1(x_1 - x_2) + x_2(y_2 - y_1) - y_2(x_2 - x_1)] = 0. \tag{45.44}$$

The states of a many-electron system may be classified by their total angular momentum or orbital spin $\mathbf{m}^2 = \hbar^2 l(l+1)$, $l = 0, 1, 2, \cdots$, as S-, P-, D-states, and so forth. For S-states we then only obtain wave functions of the type $\psi = \psi(r_1, r_2, r_{12})$, symmetric or antisymmetric in r_1, r_2. For

P-states with a zero component of the angular momentum in the spin direction, the wave function will have the general form

$$\psi = \Psi(r_1, r_2, r_{12}) \cos \vartheta_2 \pm \Psi(r_2, r_1, r_{12}) \cos \vartheta_1. \tag{45.45}$$

For D-states, it takes the form

$$\psi = \Psi P_2(\cos \vartheta_2) + \Phi(\tfrac{3}{2} \cos \vartheta_1 \cos \vartheta_2 - \tfrac{1}{2} \cos \vartheta)$$
$$\pm [\bar{\Psi} P_2(\cos \vartheta_1) + \bar{\Phi}(\tfrac{3}{2} \cos \vartheta_1 \cos \vartheta_2 - \tfrac{1}{2} \cos \vartheta)]. \tag{45.46}$$

Ψ and Φ denote functions of the same three variables as in (45.45), and $\bar{\Psi}$, $\bar{\Phi}$ the corresponding functions transposed in r_1 and r_2. In the following we shall restrict ourselves to considering the ground state which is a symmetric S-state.

Coordinate Systems

It follows from the equation

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos \vartheta \tag{45.47}$$

that the wave function for S-states may also be expressed in terms of the three variables r_1, r_2, and ϑ. The equation may then be written in a form corresponding to (45.14), that is,

$$\left(\nabla_1^2 + \nabla_2^2 + \frac{E}{4} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{Zr_{12}}\right)\psi = 0, \tag{45.48}$$

or even to (45.35) with an arbitrary dilation factor. The Laplacians here become very simple, namely,

$$\nabla_i^2 = \frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i}\frac{\partial}{\partial r_i} + \frac{1}{r_i^2}\frac{1}{\sin \vartheta}\frac{1}{\partial \vartheta} \sin \vartheta \frac{\partial}{\partial \vartheta}. \tag{45.49}$$

From this it is evident that the wave equation becomes self-adjoint upon multiplication by the density function $r_1^2 r_2^2 \sin \vartheta$, so that we may take

$$d\tau = r_1^2 r_2^2 \sin \vartheta \, dr_1 \, dr_2 \, d\vartheta, \tag{45.50}$$

as the element of volume for our three coordinates. When transforming to the coordinates r_1, r_2, r_{12}, we utilize the fact that

$$r_{12} \, dr_{12} = r_1 r_2 \sin \vartheta \, d\vartheta \tag{45.51}$$

by (45.47) and keep r_1 and r_2 fixed, thus obtaining

$$d\tau = r_1 r_2 r_{12} \, dr_1 \, dr_2 \, dr_{12}. \tag{45.52}$$

In order to determine the Laplacians in this system it is most convenient to calculate first the expression $(\nabla_1 \psi)^2 + (\nabla_2 \psi)^2$. Introducing the notation

$\mathbf{r}_1/r_1 = \hat{\mathbf{r}}_1$, and so on, we have

$$\nabla_1\psi = \hat{\mathbf{r}}_1 \frac{\partial\psi}{\partial r_1} + \hat{\mathbf{r}}_{12} \frac{\partial\psi}{\partial r_{12}}\,; \tag{45.53}$$

squaring and adding the corresponding $(\nabla_2\psi)^2$ then leads to

$$(\nabla_1\psi)^2 + (\nabla_2\psi)^2 = \left(\frac{\partial\psi}{\partial r_1}\right)^2 + \left(\frac{\partial\psi}{\partial r_2}\right)^2 + 2\left(\frac{\partial\psi}{\partial r_{12}}\right)^2 + \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial\psi}{\partial r_1}\frac{\partial\psi}{\partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}} \frac{\partial\psi}{\partial r_2}\frac{\partial\psi}{\partial r_{12}}\,. \tag{45.54}$$

Transforming to the coordinates

$$s = r_1 + r_2, \qquad t = r_2 - r_1, \qquad u = r_{12}, \tag{45.55}$$

we find that

$$d\tau = \tfrac{1}{8}(s^2 - t^2)u\, ds\, dt\, du, \tag{45.56}$$

while the gradient squares become

$$(\nabla_1\psi)^2 + (\nabla_2\psi)^2 = 2\left[\left(\frac{\partial\psi}{\partial s}\right)^2 + \left(\frac{\partial\psi}{\partial t}\right)^2 + \left(\frac{\partial\psi}{\partial u}\right)^2 + \frac{2}{u(s^2 - t^2)} \times \left(2s(u^2 - t^2)\frac{\partial\psi}{\partial s}\frac{\partial\psi}{\partial u} + 2t(s^2 - u^2)\frac{\partial\psi}{\partial t}\frac{\partial\psi}{\partial u}\right)\right]. \tag{45.57}$$

The limits of integration are here

$$-u \leqq t \leqq u, \qquad 0 \leqq u \leqq s, \qquad 0 \leqq s \leqq \infty, \tag{45.58}$$

or $0 \leqq t \leqq u$ if we restrict ourselves to half of the coordinate region.

A possible variant of this coordinate system would be z, u, t, with

$$z = s - u \tag{45.59}$$

which yields the element of volume

$$d\tau = \tfrac{1}{8}[(z + u)^2 - t^2]u\, dz\, dt\, du \tag{45.60}$$

and the gradient squares

$$(\nabla_1\psi)^2 + (\nabla_2\psi)^2 = \frac{2}{[(z + u)^2 - t^2]u}\left\{2z[(z + u)u + t^2]\frac{\partial\psi}{\partial z}\left(\frac{\partial\psi}{\partial z} - \frac{\partial\psi}{\partial u}\right) + [(z + u)^2 - t^2]\left[\left(\frac{\partial\psi}{\partial u}\right)^2 + \left(\frac{\partial\psi}{\partial t}\right)^2\right] + 2tz(z + 2u)\frac{\partial\psi}{\partial t}\left(\frac{\partial\psi}{\partial u} - \frac{\partial\psi}{\partial z}\right)\right\}. \tag{45.61}$$

This system has the advantage that the limits of integration for z and u are independent of each other,

$$0 \leqq z \leqq \infty, \qquad 0 \leqq u \leqq \infty, \tag{45.62}$$

while those for t are as before.

Finally we might put

$$\begin{aligned} x &= \tfrac{1}{2}(u - t) = \tfrac{1}{2}(r_{12} + r_1 - r_2), \\ y &= \tfrac{1}{2}(u + t) = \tfrac{1}{2}(r_{12} + r_2 - r_1), \\ z &= s - u = r_1 + r_2 - r_{12}. \end{aligned} \tag{45.63}$$

These are the so-called perimetric coordinates. They have the advantage that all limits of integration become independent of each other,

$$0 \leqq x \leqq \infty, \qquad 0 \leqq y \leqq \infty, \qquad 0 \leqq z \geqq \infty. \tag{45.64}$$

The reverse transformations are

$$\begin{aligned} s &= x + y + z, & u &= x + y, & t &= y - x, \\ r_1 &= x + \tfrac{1}{2}z, & r_2 &= y + \tfrac{1}{2}z, & r_{12} &= x + y \end{aligned} \tag{45.65}$$

and the element of volume in perimetric coordinates is

$$d\tau = (x + y)(x + \tfrac{1}{2}z)(y + \tfrac{1}{2}z)\, dx\, dy\, dz. \tag{45.66}$$

The gradient squares may be found by substituting

$$\frac{\partial\psi}{\partial u} = \frac{1}{2}\frac{\partial\psi}{\partial x} + \frac{1}{2}\frac{\partial\psi}{\partial y}, \qquad \frac{\partial\psi}{\partial t} = -\frac{1}{2}\frac{\partial\psi}{\partial x} + \frac{1}{2}\frac{\partial\psi}{\partial y} \tag{45.67}$$

into (45.61). This yields

$$\begin{aligned} (\nabla_1\psi)^2 + (\nabla_2\psi)^2 = {} & \frac{1}{(x + y)(x + \frac{1}{2}z)(y + \frac{1}{2}z)} \\ & \times \left\{ [2(x^2 + y^2) + (x + y)z]z\left(\frac{\partial\psi}{\partial z}\right)^2 \right. \\ & + \left[(x + y)(y + z) + \frac{1}{2}z^2\right]x\left(\frac{\partial\psi}{\partial x}\right)^2 \\ & + \left[(x + y)(x + z) + \frac{1}{2}z^2\right]y\left(\frac{\partial\psi}{\partial y}\right)^2 \\ & \left. - (2x + z)xz\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial z} - (2y + z)yz\frac{\partial\psi}{\partial y}\frac{\partial\psi}{\partial z} \right\}. \end{aligned} \tag{45.68}$$

The unperturbed wave function is

$$\psi_0 = \exp\left[-\tfrac{1}{2}(r_1 + r_2)\right] = \exp\left(-\tfrac{1}{2}s\right) = \exp\left[-\tfrac{1}{2}(x + y + z)\right] \tag{45.69}$$

regardless of whether we introduce the dilation factor k or not. It is convenient to take this function as a common factor of all auxiliary functions employed in our calculations. Thus writing

$$\psi = \psi_0 \Psi, \tag{45.70}$$

we find the gradient squares in (45.37),

$$\begin{aligned}\int (\nabla_i \psi)^2 \, d\tau &= \int \psi_0^2 (\nabla_i \Psi)^2 \, d\tau + \int (\nabla_i \Psi^2) \psi_0 \nabla \psi_0 \, d\tau + \int \Psi^2 (\nabla \psi_0)^2 \, d\tau \\ &= \int \psi_0^2 (\nabla_i \Psi)^2 \, d\tau - \int \Psi^2 \psi_0 \nabla_i^2 \psi_0 \, d\tau \\ &= \int \psi_0^2 (\nabla_i \Psi)^2 \, d\tau + \int \Psi^2 \psi_0^2 \left(-\frac{1}{4} + \frac{1}{r_i}\right) d\tau. \end{aligned} \tag{45.71}$$

Putting $i = 1, 2$ and adding the two resulting equations together, we obtain

$$M = M' + L - \tfrac{1}{2}N, \qquad M' = \int e^{-s}\left[(\nabla_1 \Psi)^2 + (\nabla_2 \Psi)^2\right] d\tau. \tag{45.72}$$

This formula will in general considerably facilitate the rather involved calculation of M.

46. NUMERICAL EXAMPLES

The Ground State of the Helium Atom

The hitherto most accurate experimentally measured value for the energy of ionization for helium in the ground state is

$$J_{\text{exp}} = 198310.82 \pm 0.15 \text{ cm}^{-1}. \tag{46.1}$$

This corresponds to a ground state energy of

$$E_{\text{exp}} = -5.80756979 \text{ Ry} \tag{46.2}$$

or

$$E_{\text{exp}} = -1.45189245, \tag{46.3}$$

measured in units of Z^2 Ry. The experimental inaccuracy corresponds to 34 units in the last decimal of the energy value (46.3).

Our most primitive perturbation treatment, not using any dilation factor, yielded the result

$$E = -1.375. \tag{46.4}$$

Introducing the dilation factor $k = 1 - \frac{5}{16}(1/Z)$, we found

$$E = -1.42382. \tag{46.5}$$

It seems natural to expect a term of the form

$$\Psi = (1 - \alpha)^{5/2} e^{\frac{1}{2}\alpha u}, \tag{46.6}$$

to appear in the wave function; the first part of (46.6) has been inserted for purposes of normalization only. Such a term would tend to favor large distances $u = r_{12}$ between the electrons corresponding to the mutual repulsion of the latter. It represents a kind of polarization. If we now insert this term into our formulas, and—because of the symmetry—integrate over only half of the coordinate region, we obtain

$$\begin{aligned} N &= 2 + 1.5(1 - \alpha) + 0.5(1 - \alpha)^2, \\ L &= 3(1 - \alpha) + (1 - \alpha)^2, \\ M &= L - \tfrac{1}{2}(1 - \alpha^2)N, \\ L' &= 0.5(1 - \alpha) + 0.5(1 - \alpha)^2 + 0.25(1 - \alpha)^3. \end{aligned} \tag{46.7}$$

The actual calculations are very simple. For $\alpha = 0$ we arrive at the value (46.5), and $\alpha = 0.1$ and 0.2 enable us to localize the optimal value to $\alpha = 0.13 - 0.14$ with a fairly good approximation for the energy also. Then $\alpha = 0.14$ yields

$$\begin{aligned} N &= 3.6598, \qquad L = 3.3196, \\ M &= 1.525566, \qquad \tfrac{1}{2}L' = 0.479407, \\ E &= -1.444800. \end{aligned} \tag{46.8}$$

Another way to consider the problem is to observe that the electrons will usually be at different distances from the nucleus. The central (nuclear) attraction will then on the average be considerably decreased for the outer electron, and correspondingly increased for the inner electron. This effect may, to a certain extent, be taken into account by choosing

$$\Psi = (1 - \beta^2)^{3/2} \cosh \tfrac{1}{2}\beta t. \tag{46.9}$$

We then find

$$\begin{aligned} N &= 2 + 2(1 - \beta^2)^3 = L, \\ M &= \tfrac{1}{2}N + \beta^2[1 - (1 - \beta^2)^3], \\ L' &= \tfrac{1}{2}(1 - \beta^2) + \tfrac{1}{8}(1 - \beta^2)^2 + \tfrac{5}{8}(1 - \beta^2)^3. \end{aligned} \tag{46.10}$$

Clearly β^2, rather than β, should here be chosen as the parameter. Putting

$\beta^2 = 0.1$, we readily obtain

$$N = L = 3.458, \qquad M = 1.7561, \qquad \tfrac{1}{2}L' = 0.503437, \qquad E = -1.437515 \tag{46.11}$$

which is close to the minimum

$$E = -1.4377, \qquad \beta = 0.3, \qquad \beta^2 = 0.09. \tag{46.12}$$

If we combine these two methods, the gain is somewhat less than expected; we then find that

$$E = -1.4497. \tag{46.13}$$

We shall now compare these methods with another, which is less easy to visualize but nevertheless superior to those just discussed, due to its simplicity and flexibility. We write

$$\Psi = 1 + c_1 u + c_2 t^2. \tag{46.14}$$

It is then tacitly assumed that we, as before, employ the dilation factor k as our last variation; this corresponds to putting

$$E = -\frac{(L - L'/Z)^2}{NM}. \tag{46.15}$$

Using the formulas (45.55) to (45.57) and (45.72), it then follows that

$$\begin{aligned} N = 4 &+ (2 \times 17.5c_1) + (2 \times 24c)_2 \\ &+ 96c_1^2 \quad + (2 \times 154c_1c_2) \\ &\qquad + 576c_2^2, \end{aligned} \qquad \begin{aligned} L = 4 &+ (2 \times 15c_1) + (2 \times 24c_2) \\ &+ 72c_1^2 \quad + (2 \times 140c_1c_2) \\ &\qquad + 576c_2^2, \end{aligned} \tag{46.16}$$

$$\begin{aligned} M = 2 &+ (2 \times 6.25c_1) + (2 \times 12c_2) \\ &+ 32c_1^2 \quad + (2 \times 73c_1c_2) \\ &\qquad + 480c_2^2, \end{aligned} \qquad \begin{aligned} \tfrac{1}{2}L' = 0.625 &+ (2 \times 2c_1) + (2 \times 2.25c) \\ &+ 8.75c_1^2 + (2 \times 12c_1c_2) \\ &\qquad + 39c_2^2. \end{aligned}$$

If we vary c_1 and c_2 separately, we find, for $c_2 = 0$, $c_1 = 0.1$, that

$$E = -1.4456, \tag{46.17}$$

and, for $c_1 = 0$, $c_2 = 0.012$, that

$$E = -1.4384. \tag{46.18}$$

Both these results show noticeable improvement from (46.8) and (46.12), respectively.

The improvement becomes still greater if both terms are varied simultaneously. With $c_1 = 0.08$ and $c_2 = 0.01$ we obtain

$$E = -1.45122, \tag{46.19}$$

relative to (46.13); this evidently corresponds to an addition (practically) of the two separate improvements discussed above.

Comparing with the experimental result (46.3), we see that the error already appears as far out as in the fourth decimal. A further improvement results from inclusion of the term s and the second-degree terms s^2 and u^2; this yields

$$E = -1.45162, \tag{46.20}$$

where the inaccuracy is now only two units in the fourth decimal.

When successively more terms from the chosen basis set are included, the energy will converge toward the exact eigenvalue for the Hamiltonian operator, provided that the basis set is complete. Thus, using 204 such terms, we find

$$E_{NR} = -1.45186218, \tag{46.21}$$

where the deviation from the exact eigenvalue (which would result from the inclusion of an infinite number of terms in the wave function) is less than one unit in the last decimal. This value does not accord with the experimentally observed (46.3); this is because it is only the so-called nonrelativistic energy of the ground state. It is necessary to take into account certain corrective energy terms, such as the mass polarization correction, various relativistic effects, and the Lamb shift. Using the same 204 terms as above, these have been calculated to have the following values:

$$\begin{aligned} E_M &= 0.00001090, \\ E_R &= -0.00005197, \\ E_L &= 0.00001094. \end{aligned} \tag{46.22}$$

If these are added to the nonrelativistic energy (46.21), we obtain the total theoretically predicted energy

$$E_{\text{theor}} = -1.45189231 \tag{46.23}$$

in satisfactory agreement with (46.3).

The Negative Hydrogen Ion

The above-mentioned, second-order corrections obtained by variational methods are sufficient to demonstrate the stability—and hence the existence—of the negative hydrogen ion, H^-, with two electrons bound to the singly charged nucleus, $Z = 1$.

The first-order approximation yields $E = -\frac{121}{128}$, measured in units of Z^2 Ry (or in Rydberg units, which is the same in this case). Thus this approximation is not sufficient, since we must go down below -1 Ry in order to demonstrate stability.

The second-order approximation, on the other hand, leads to

$$\begin{aligned} E &= -1.0176, \qquad c_1 = 0.3, \qquad c_2 = 0, \\ E &= -1.0238, \qquad c_1 = 0, \qquad c_2 = 0.06. \end{aligned} \tag{46.24}$$

At the third order we obtain the still more accurate energy value

$$E = -1.0506, \qquad c_1 = 0.2, \qquad c_2 = 0.05. \tag{46.25}$$

Using the same 204 terms as previously employed in the helium problems, we find the following values for the nonrelativistic energy and the correction mentioned above:

$$\begin{aligned} E_{NR} &= -1.0555015, \\ E_M &= 0.0000358, \\ E_R &= -0.0000105, \\ E_L &= 0.0000025. \end{aligned} \tag{46.26}$$

The total theoretically computed energy value thus becomes

$$E_{\text{theor}} = -1.0554737, \tag{46.27}$$

where the inaccuracy, by our calculations, amounts to one unit in the sixth decimal. This inaccuracy is considerably greater than that which appeared in the corresponding helium problem. This is because the numerical calculations here converge much more slowly, due to the smaller value of Z.

Experimental values for the energy of the negative hydrogen ion have not, to date, been determined. Apart from the possible existence of this ion in certain (alkali) hydride compounds, it appeared at one time to be of hardly more than theoretical academic interest, since its lifetime would necessarily be extremely short, even under the most perfect vacuum conditions feasible in a laboratory. At present, however, the negative hydrogen ion plays a prominent role in the study of astrophysical processes, in particular of the absorption conditions in the solar atmosphere.

The Helium Isoelectronic Sequence

It is evident from the preceding theory of the variational method that if we wish to compute the energy for several values of Z, we must solve the secular equation anew every time, even if we consider only one particular state.

In this case it may be an advantage to employ instead a perturbation method, that is, the special variational perturbation method described in

(40.20) to (40.36), using Z^{-1} as the perturbation parameter. [Compare (45.14).]

Thus we write the energy E of the system and its total state function Φ, as

$$E = \sum_{n=0}^{\infty} E_n Z^{-n}, \tag{46.28}$$

$$\Phi = \sum_{n=0}^{\infty} \varphi_n Z^{-n}, \tag{46.29}$$

where

$$\varphi_n = \sum_{i=1}^{m} c_{ni} \psi_i. \tag{46.30}$$

We note that if successively more functions Φ_n are included in the expansion (46.29)—which in turn yields successively more energy coefficients E_n in the expansion (46.28)—the approximate energy E of (46.28) will converge toward the same value as would have been obtained by means of the variational method, using the same m functions ψ_i from the given basis set. However, we have now expressed the energy as a function of Z, and may thus insert any desired value of this parameter.

We have listed in Table 7-1 the first 12 energy coefficients for the state $(1s)^2\ ^1S$. These may be utilized to calculate the energy for all values of Z, that is, for the complete isoelectronic sequence of helium. We have also included the energy for the first 10 terms of this sequence. The computation of these values has been based on a more complete list of energy coefficients.

Table 7-1

n	E_n	Z	E
0	−2.0	1	−1.0555018
1	1.25	2	−1.45186219
2	−0.31533287	3	−1.61775854
3	0.01739810	4	−1.70694578
4	−0.00177747	5	−1.76247773
5	−0.00207272	6	−1.80034703
6	−0.00122588	7	−1.82781409
7	−0.00074436	8	−1.84864360
8	−0.00048575	9	−1.86498055
9	−0.00033131	10	−1.87813613
10	−0.00023236		
11	−0.00016660		

CHAPTER 8

Scattering Problems

47. SCATTERING OF ELECTROMAGNETIC RADIATION IN AN ATOM

Semiclassical Treatment of the Electromagnetic Scattering Problem

In the preceding chapter we have seen how certain radiation problems, such as emission and absorption, may be partly treated in a semiclassical fashion. The method consists of calculating the disturbance in an atom due to the forces originating in the radiation field. However, certain aspects of these problems, such as spontaneous emission of radiation, is not describable by this method; one must then fall back on intuitive arguments of correspondence, like Einstein's deduction of Planck's law of radiation, in order to obtain plausible expressions for processes of this type.

If the said method is applied to scattering problems, one must here also expect it to break down in certain areas. In analogy with the fact that the phenomenon of spontaneous emission remained an unsolved problem, it is not surprising that the treatment of so-called incoherent scattering meets with particular difficulties. This phenomenon appears when the radiation exchanges energy with the atoms, in connection with quantum transitions in the latter.

The difficulty is that, while we may readily describe the action of the electromagnetic field on the atom, it is not so easy to establish satisfactory expressions for the reaction of the atom back on the radiation field. However, we are not completely destitute in this respect, since Maxwell's equations for the emission of radiation from accelerated (for instance, oscillating) charges will help us make some headway. As we have seen, an atom in a radiation field will exhibit both free (transient) and forced oscillations, the latter with the frequency of the incident radiation. We made use of this circumstance in the determination of the atomic oscillatory dipole moment and its dependence on the frequency. Moreover we were able to employ this dipole moment in

our discussion of the coherent scattering of long-wave radiation. It is therefore of considerable interest to explore how far it is possible to proceed in the treatment of scattering problems by means of such—somewhat more intuitively visualizable—semiclassical considerations.

Electromagnetic Elementary Waves from an Atom

Let us assume that an atom is in a given state, characterized by a wave function u, in which it exhibits a change in the charge density $\rho = \rho(\mathbf{r}, t)$. If the charge is not to be annihilated, a current density $\mathbf{j} = \mathbf{j}(\mathbf{r}, t)$ must then also obtain; and these two quantities must be connected by the continuity equation

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \mathbf{j} = 0. \tag{47.1}$$

It seems natural to try to describe the reaction of the atom back on the radiation field by calculating the radiation which, by electromagnetic theory, must be emitted from an atom with these charge and current densities. This radiation may be determined by means of the electromagnetic potentials

$$\begin{aligned} \mathbf{A}(\mathbf{r}, t) &= \frac{1}{c} \int \frac{\mathbf{j}'(\mathbf{r}', t')}{|\mathbf{r} - \mathbf{r}'|} d\tau', \\ \Phi(\mathbf{r}, t) &= \int \frac{\rho(\mathbf{r}', t')}{|\mathbf{r} - \mathbf{r}'|} d\tau'. \end{aligned} \tag{47.2}$$

Here $\mathbf{r}$ is the position vector to the field point from a fixed origin (which is assumed to be the center of the atomic nucleus), $\mathbf{r}'$ the corresponding vector to the element of the volume $d\tau'$, and

$$t' = t - \frac{|\mathbf{r} - \mathbf{r}'|}{c} \tag{47.3}$$

the so-called retarded time.

When calculating the field at great distances from the origin, the denominators of (47.2) may be replaced by r, and t' may be written

$$t' = t - \frac{r}{c} + \frac{\mathbf{n}\mathbf{r}'}{c}, \qquad \mathbf{n} = \frac{\mathbf{r}}{r}, \tag{47.4}$$

where $\mathbf{n}$ denotes the direction of the emitted radiation. This yields

$$\begin{aligned} \mathbf{A}(\mathbf{r}, t) &= \frac{1}{cr} \int \mathbf{j}(\mathbf{r}', t') d\tau', \\ \Phi(\mathbf{r}, t) &= \frac{1}{r} \int \rho(\mathbf{r}', t') d\tau'. \end{aligned} \tag{47.5}$$

Furthermore we always have $\mathbf{H} = \mathbf{n} \times \mathbf{E}$ in the wave zone; hence it is only necessary to determine $\mathbf{E}$, which is given by

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t} - \nabla\Phi, \qquad \text{where} \qquad \operatorname{div}\mathbf{A} + \frac{1}{c}\frac{\partial \Phi}{\partial t} = 0. \tag{47.6}$$

Let div′ denote differentiations that are also to be performed through t'. (Compare Problem 1 at the end of this section.) Equation (47.1) is then equivalent to

$$\dot{\rho}(\mathbf{r}', t') - \frac{1}{c}\mathbf{n}\dot{\mathbf{j}}(\mathbf{r}', t') = -\operatorname{div}'\mathbf{j}(\mathbf{r}', t'). \tag{47.7}$$

Omitting—as is usual in the wave zone—differentiations of the denominator r in (47.5), we find by means of (47.7) that the last equation (47.6) is satisfied, since the volume integral of the term div′ $\mathbf{j}$ vanishes. We now calculate $\mathbf{E}$, finding by means of $\nabla\rho = -(\mathbf{n}/c)\dot{\rho}$ that

$$\mathbf{E} = -\frac{1}{c^2 r}\int(\dot{\mathbf{j}} - c\mathbf{n}\dot{\rho})\, d\tau' = -\frac{1}{c^2 r}\int[\dot{\mathbf{j}} - \mathbf{n}(\mathbf{n}\dot{\mathbf{j}})]\, d\tau', \tag{47.8}$$

since the integral of the additional term $\mathbf{n}$ div′ $\mathbf{j}$ also vanishes.

Introducing the new vector potential

$$\mathbf{A}'(\mathbf{r}, t) = \mathbf{A} - (\mathbf{n}\mathbf{A})\mathbf{n} = \mathbf{n} \times (\mathbf{A} \times \mathbf{n}), \tag{47.9}$$

we may write

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}'}{\partial t}, \qquad \operatorname{div}\mathbf{A}' = 0, \tag{47.9a}$$

Thus we have expressed the electric field in terms of a divergence-free vector potential $\mathbf{A}'$, which differs from the vector potential $\mathbf{A}$ in (47.5) only in strength and direction. If its direction is characterized by a unit vector $\mathbf{e}_0$, the unit vector $\mathbf{e}$ in the polarization direction of $\mathbf{A}'$ will be determined by

$$\mathbf{e}\sin\Theta = \mathbf{n} \times (\mathbf{e}_0 \times \mathbf{n}). \tag{47.10}$$

Multiplication by $\mathbf{e}$ yields, since $\mathbf{e}\mathbf{n} = 0$,

$$\sin\Theta = \mathbf{e}\mathbf{e}_0 = \cos\vartheta', \tag{47.11}$$

where ϑ' is the angle between the two vectors of polarization; Θ and ϑ' are thus complementary angles.

Charge and Current Densities for an Atom in an Electromagnetic Field

For a one-electron atom we may define the densities of charge and current by the equation

$$\rho = -eu^*u, \qquad \mathbf{j} = -e\mathbf{v}, \qquad \mathbf{v} = \operatorname{Re} u^*\dot{\mathbf{r}}u, \tag{47.12}$$

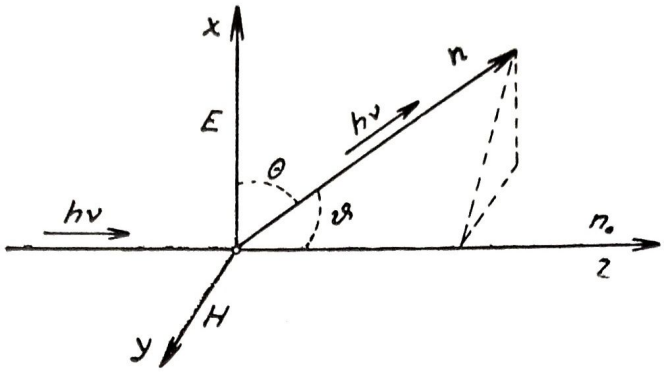

Fig. 8-1. Scattering of coherent electromagnetic radiation from an atom.

where $\mathbf{j}$ and $\mathbf{v}$ are the current densities of electric charge and of electrons, respectively. The term $\dot{\mathbf{r}}$ is the velocity operator defined by

$$\dot{\mathbf{r}} = \frac{\partial H}{\partial \mathbf{p}} = \frac{1}{m_0}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}_0\right), \tag{47.13}$$

where $\mathbf{A}_0$ is the vector potential for the incident electromagnetic waves.

Let us assume that $\mathbf{A}_0$ has the form

$$\mathbf{A}_0 = \mathbf{e}_0 A_0 \cos(\mathbf{k}_0\mathbf{r} - \omega t) = \mathbf{e}_0 A_0 \operatorname{Re} e^{i(\mathbf{k}_0\mathbf{r}-\omega t)}, \tag{47.14}$$

where $\mathbf{k}_0 = k\mathbf{n}_0$, $k = \omega/c = 2\pi/\lambda$; $\mathbf{n}_0$ may point in, say, the z-direction and $\mathbf{e}_0$ in the x-direction (compare Fig. 8-1). Even for an atom in a simple state $u = u_n$, the last term of (47.13) will give rise to an oscillating current density; on the other hand, the first term $\mathbf{p}$ requires a composite state in order to have such an effect. Such a composite state will be produced, since the coefficients will attain an oscillatory character as soon as the external field $\mathbf{A}_0$ becomes operative.

We have found earlier that the perturbation energy is in this case,

$$H' = \frac{e}{m_0 c}\mathbf{A}_0\mathbf{p} + \frac{e^2}{m_0 c^2}\mathbf{A}_0^2. \tag{47.15}$$

As previously, we shall omit the last term of (47.15) in our calculation of the coefficients $c_m(t)$.

Coherent Scattering of Short-Wave Radiation. Atomic Form Factors

We shall begin with the last term of (47.13), since this does not require the laborious task of calculating the coefficients $c_m(t)$. First of all, we obtain a current vector

$$\frac{1}{c}\mathbf{j} = -r_0 A_0 \mathbf{e}_0 \operatorname{Re} u^* u e^{i\mathbf{k}_0\mathbf{r}-i\omega t}, \qquad r_0 = \frac{e^2}{m_0 c^2}. \tag{47.16}$$

Here we replace $\mathbf{r}$ by $\mathbf{r}'$ and ωt by $\mathbf{kr} + \omega[t - (r/c)]$. The vector potential of the secondary wave in the direction $\mathbf{n}$ may then be expressed by

$$rA' = -r_0 A_0 \mathbf{e}(\mathbf{e}\mathbf{e}_0)[e^{i(\mathbf{k}_0-\mathbf{k})\mathbf{r}}]_{nn} \operatorname{Re} e^{-i\omega(t-r/c)}. \tag{47.17}$$

The quantity

$$f_{nn}(K) = (e^{i\mathbf{K}\mathbf{r}})_{nn} = \int e^{i\mathbf{K}\mathbf{r}} |\psi_n|^2 \, d\tau, \qquad \mathbf{K} = \mathbf{k}_0 - \mathbf{k}, \tag{47.18}$$

is called the *atomic form factor* for coherent scattering of short-wave electromagnetic radiation. It is easily shown that it may be written, for a spherically symmetric S-state u_n, as

$$f_{nn}(K) = \int \frac{\sin Kr}{Kr} |\psi_n|^2 \, d\tau, \qquad K = |\mathbf{k}_0 - \mathbf{k}| = 2k \sin\frac{\vartheta}{2} = \frac{4\pi}{\lambda} \sin\frac{\vartheta}{2}; \tag{47.19}$$

consequently it is real. For formal reasons, however, we note that if it were complex, the amplitude of the spherical wave (47.17) would be proportional to $|f_{nn}(K)|$. Hence we write for the differential scattering cross section,

$$\sigma(\vartheta) = f^2(\vartheta) = r_0^2(\mathbf{e}\mathbf{e}_0)^2 |f_{nn}(K)|^2, \qquad f(\vartheta) = -\frac{rA'}{A_0}. \tag{47.20}$$

Strictly speaking, the $\sigma(\vartheta)$ in this formula also depends on φ, the angle between the planes $(\mathbf{e}_0, \mathbf{n}_0)$ and $(\mathbf{n}, \mathbf{n}_0)$. The dependence is expressed by the factor $(\mathbf{e}e_0)^2$ which varies between $\cos^2\vartheta$ and unity. For unpolarized radiation it has the mean value

$$\overline{(\mathbf{e}\mathbf{e}_0)^2} = \tfrac{1}{2}(1 + \cos^2\vartheta) \tag{47.21}$$

which is the well-known Thomson factor; in this case we may also write

$$\sigma(\vartheta) = \sigma_T(\vartheta) |f_{nn}(K)|^2, \qquad \sigma_T(\vartheta) = r_0^2 \frac{1 + \cos^2\vartheta}{2}. \tag{47.22}$$

The last quantity may be referred to as the Thomson scattering cross section of free electrons with respect to electromagnetic radiation.

The Directional Distribution of Short-Wave Radiation

The quantity K in (47.19) depends both on the wavelength λ and the scattering angle ϑ. For $\vartheta = 0$ or $\lambda \to \infty$ we have $K = 0$, so that the atomic form factor becomes unity. For increasing ϑ it decreases, the more rapidly the smaller the wavelengths. For short-wave radiation the scattering therefore exhibits a marked directional dependence, apart from the Thomson factor

which is of secondary importance. The scattering is strongest in the forward direction, relative to the incident radiation.

Incoherent Scattering of Short-Wave Radiation. Sum Rule for the Total Scattering

The incoherent scattering may not be treated in the above fashion. However, it seems natural to expect it to be expressible by means of an atomic form factor for incoherent scattering $f_{mn}(K)$ obtainable from (47.18) by the substitution of $\psi_m^*\psi_n$ for $|\psi_n|^2$; thus

$$f_{mn}(K) = \int e^{i\mathbf{Kr}} \psi_m^* \psi_n \, d\tau. \tag{47.23}$$

This refers to the transition $u_n \to u_m$ which gives rise (by the energy law) to a change in the energy of the scattered photons, and hence also to a change of the wavelength. This energy change is hv_{mn}; since u_n is usually the state of lowest energy, the scattered light must have a greater wavelength.

This will also affect the quantity $K = |\mathbf{k}_0 - \mathbf{k}|$, since $|\mathbf{k}| < |\mathbf{k}_0|$. For radiation of very short wavelengths (such as X-rays), however, this change may be neglected to a high accuracy.

Thus we write, tentatively,

$$\sigma_{\text{incoh}}(\vartheta) = \sigma_T(\vartheta) \, |f_{mn}(K)|^2 \tag{47.24}$$

for the differential scattering cross section for incoherent radiation. By the rules of matrix multiplication, however, we have

$$\sum_m |f_{mn}(K)|^2 \sum_m (e^{-i\mathbf{Kr}})_{nm} (e^{-i\mathbf{Kr}})_{mn} = (e^{-i\mathbf{Kr}} \cdot e^{i\mathbf{Kr}})_{nn} = 1. \tag{47.25}$$

Hence it follows that

$$\sigma_{\text{coh}}(\vartheta) + \sigma_{\text{incoh}}(\vartheta) = \sigma_T(\vartheta), \tag{47.26}$$

that is, we obtain the plausible result that the sum of coherent and incoherent scattering of short-wave (high-energy) radiation in a one-electron problem is equal to the Thomson scattering for a free electron. This would seem to furnish the best support for the—at present purely heuristic—equations (47.23) and (47.24).

Coherent Scattering of Long-Wave Radiation

For long-wave radiation the first term in (47.13) must also be taken into account; we may then determine the coefficients $c_m(t)$ by means of (47.14), (47.15), and (42.8). For brevity we write

$$p_0 = \mathbf{e}_0\mathbf{p}, \qquad p = \mathbf{ep} \tag{47.27}$$

for the components of momentum along the two vectors of polarization.

By a procedure similar to that described above using (47.14) and (47.15) we arrive at the somewhat complicated expression

$$\frac{e}{c}c_m(t) = r_0\frac{2\pi}{h}\cdot\frac{A_0}{2}\left\{(e^{i\mathbf{k}_0\mathbf{r}}p_0)_{mn}\frac{1-e^{i(\omega_{mn}-\omega)t}}{\omega_{mn}-\omega} + (e^{-i\mathbf{k}_0\mathbf{r}}p_0)_{mn}\frac{1-e^{i(\omega_{mn}+\omega)t}}{\omega_{mn}+\omega}\right\} \tag{47.28}$$

Multiplying $c_m(t)$ by the time-dependent factor $e^{-i\omega_{mn}t}$ in $u_m^*u_n$, two terms of the form $e^{-i\omega_{mn}t}$ appear which are of no interest for the scattering problem considered. We therefore retain only the two terms of the form $e^{\pm i\omega t}$ and introduce the abbreviations,

$$\begin{aligned} p_0^+ &= e^{i\mathbf{k}_0\mathbf{r}}p_0, \qquad & p_0^- &= e^{-i\mathbf{k}_0\mathbf{r}}p_0, \\ p^+ &= e^{i\mathbf{k}\mathbf{r}}p, \qquad & p^- &= e^{-i\mathbf{k}\mathbf{r}}p, \end{aligned} \tag{47.29}$$

to obtain

$$-\frac{e}{c}e^{-\omega_{mn}t}c_m(t) = r_0\frac{2\pi}{h}\cdot\frac{A_0}{2}\left[\frac{(p_0^+)_{mn}e^{-i\omega t}}{\omega_{mn}-\omega} + \frac{(p_0^-)_{mn}e^{i\omega t}}{\omega_{mn}+\omega}\right]. \tag{47.30}$$

We must now put

$$\begin{gathered} e^{-i\omega t}\to e^{-i\mathbf{k}\mathbf{r}'-i\omega T}, \qquad e^{i\omega t}\to e^{i\mathbf{k}\mathbf{r}'+i\omega T}, \\ T = t-\frac{r}{c} \end{gathered} \tag{47.31}$$

in (47.30), multiply by $\frac{1}{m_0}\psi_n^*p\psi_m\,d\tau'$ and integrate [compare (47.5), (47.9), (47.12) and (47.13)]. Thereupon we multiply the corresponding expression for $e_m^*(t)$ by $\frac{1}{m_0}\psi_m^*p\psi_n\,d\tau'$ and integrate. Finally we add these two terms. It turns out, however, that these are complex conjugates, so that their sum is real; hence the Re in (47.12) is immaterial. On the other hand, we might content ourselves with considering the double of the real part of that which results from (30). In other words, we obtain

$$\frac{rA'}{A_0} = r_0\frac{2\pi}{hm_0}\operatorname{Re}\left(\frac{p_{0mn}^+p_{nm}^-e^{-i\omega T}}{\omega_{mn}-\omega} + \frac{p_{0mn}^-p_{nm}^+e^{i\omega T}}{\omega_{mn}+\omega}\right). \tag{47.32}$$

To simplify this expression as much as possible we consider the numerators of the two formulas first. Since ψ_m and ψ_n are both solutions of the Schrödinger wave equation in the absence of an atomic field, they may be chosen to be real; moreover, they are either both even or both odd with respect to reflections of the axes of the coordinate system. We find

$$(p_{0mn}^+)^* = -\int\psi_me^{-i\mathbf{k}_0\mathbf{r}}\frac{h}{2\pi i}\,\mathbf{e}_0\nabla\psi_n\,d\tau, \tag{47.33}$$

and substituting $-\mathbf{r}$ for $\mathbf{r}$,

$$(p^+_{0mn})^* = \pm \int \psi_m e^{i\mathbf{k}_0\mathbf{r}} \frac{h}{2\pi i} \mathbf{e}_0 \nabla \psi_n \, d\tau = \pm p^+_{0mn}, \tag{47.33a}$$

according as the $\psi_m\psi_n$ are even or odd. The corresponding matrix elements are thus real or purely imaginary, respectively. The same result is obtained for p^-_{nm}, p^-_{0mn} and p^+_{nm}; consequently both the numerators, apart from the factor $e^{\pm i\omega T}$, are real. This leads to

$$p^-_{0mn}p^+_{nm} = p^+_{0nm}p^-_{mn}, \tag{47.34}$$

since the two expressions are also complex conjugates. Since p_0 and $\mathbf{k}_0\mathbf{r}_0$ commute, and also p and $\mathbf{kr}$, it may be shown (by integrating in parts) that

$$p^+_{0nm} = -p^+_{0mn}, \qquad p^-_{mn} = -p^-_{nm}. \tag{47.34a}$$

Thus the two numerators are even equal in magnitude.

We now sum over all states m, which will here be denoted by i, and add the term previously obtained in (47.20). Disregarding the factor $\cos \omega T$, we then find the amplitude ratio

$$f(\vartheta) = -\frac{rA'}{A_0} = r_0\left[(\mathbf{ee}_0)f_{nn}(K) - \sum_i{}' \frac{4\pi\omega_{im}}{hm_0} \cdot \frac{p^+_{0in}p^-_{ni}}{\omega_{in}{}^2 - \omega^2}\right]$$

$$= r_0\left[(\mathbf{ee}_0)f_{nn}(K) - \sum_i{}' \frac{\omega_{in}{}^2 g_{in}}{\omega_{in}{}^2 - \omega^2}\right], \tag{47.35}$$

$$g_{in} = \frac{4\pi}{hm_0\omega_{in}} (e^{i\mathbf{k}_0\mathbf{r}}\mathbf{e}_0\mathbf{p})_{in}(e^{-i\mathbf{kr}}e\mathbf{p})_{ni}. \tag{47.35a}$$

Discussion of the Scattering Formula

Because of the simple form of the scattering phase $f(\vartheta)$ in (47.35), it seems natural to investigate the possibility of finding an organic connection between the direction-dependent oscillator strengths g_{in} and the first term $(\mathbf{ee}_0)f_{nn}(K)$ in the formula.

We may first consider the case $k \to 0$. The only matrix elements of interest are then those where $(e_0p)_{in} \neq 0$, while the other components vanish. Clearly $(\mathbf{ep})_{ni} = (\mathbf{ee}_0)(\mathbf{e}_0\mathbf{p})_{ni}$. We obtain

$$g_{in} = (\mathbf{ee}_0)f_{in}, \tag{47.36}$$

where f_{in} are the previously discussed numerical oscillator strengths satisfying the sum rule $\sum_i |f_{in}|^2 = 1$, while at the same time $f_{nn}(K) \to 1$. Thus we arrive back at exactly the same scattering formula obtained during the treatment of dispersion theory with the Thomson factor $\mathbf{ee}_0$ or $\frac{1}{2}(1 + \cos^2\vartheta)$.

In the general case $k \neq 0$ it is, unfortunately, not possible to sum the oscillator strengths g_{in} explicitly unless certain simplifications are introduced.

We may, however, write the approximate formula

$$g_{in} = \frac{2\pi i}{h}(p^-_{ni}r^+_{0in} - r^+_{ni}p^-_{0in}), \qquad r^+_0 = e^{i\mathbf{k}_0\mathbf{r}}\mathbf{e}_0\mathbf{r}. \tag{47.37}$$

[Compare (42.22) and Problem 2 at the end of Section 42.] Here we have utilized the fact that $\mathbf{e}_0\mathbf{p}$ and $\mathbf{k}_0\mathbf{r}$, being orthogonal components of the momentum and position vector, commute. However, we have disregarded the fact that the Hamiltonian does not commute with $e^{i\mathbf{k}_0\mathbf{r}}$ because of the term $1/2m_0p^2$ in H.

With these simplifying assumptions, the g_{in} may be summed. We find

$$\sum_i{}' g_{in} = \frac{2\pi i}{h}(p^-r^+_0 - r^+_0p^-)_{nn}. \tag{47.38}$$

Assuming, to the same accuracy, that p^- commutes with $e^{i\mathbf{k}_0\mathbf{r}}$, we obtain

$$\sum_i g_{in} = (\mathbf{ee}_0)(e^{i\mathbf{K}\mathbf{r}})_{nn} = (\mathbf{ee}_0)f_{nn}(K). \tag{47.38a}$$

It is evident from these considerations that both the Thomson factor and the directional dependence corresponding to $f_{nn}(K)$ appear very extensively throughout the theory for coherent scattering of electromagnetic radiation of any frequencies.

Incoherent Scattering

In the case of incoherent scattering, we must (as already mentioned) resort largely to guesswork; however, this may be supported in several ways by arguments of plausibility. The correct generalization of (47.35) is

$$f(\vartheta) = r_0\left(\frac{\omega'}{\omega}\right)^{1/2}\left|(\mathbf{ee}_0)f_{mn}(K) - \sum_i{}'\frac{2\pi}{hm_0}\left(\frac{p^+_{0in}p^-_{mi}}{\omega_{in} - \omega} + \frac{p^-_{0in}p^+_{mi}}{\omega_{im} + \omega}\right)\right|, \tag{47.39}$$

$$\omega' = \omega - \omega_{mn}, \qquad \text{or} \qquad \omega_{im} + \omega = \omega_{in} + \omega'.$$

Here, as earlier, the two numerators will be of the same magnitude; hence the two terms may be contracted to one. However, they are not real, since the quantities $\psi_i\psi_n$ and $\psi_i\psi_m$ need not have the same parity. For this reason, we may not—as was possible in the case of coherent scattering—omit the sign for the modulus.

Problem

1. Let div′ signify differentiation through t', and div differentiation only through the explicit coordinates $\mathbf{r}'$ in $\mathbf{j}(\mathbf{r}', t')$. Show that

$$\text{div}'\,\mathbf{j} = \text{div}\,\mathbf{j} + \frac{1}{c}\dot{\mathbf{n}}\mathbf{j}.$$

48. SCATTERING OF ELECTRONS IN A POTENTIAL FIELD

Atomic Potential Fields and the Born Approximation

The scattering of electrons in an atom is very similar to the scattering of electromagnetic radiation. In order to obtain some idea of this process we shall disregard any changes in the atom itself and represent it by a potential field corresponding to the nuclear charge Ze and the configuration of the Z orbital electrons. This configuration will be assumed to have a spherically symmetric statistical distribution denoted by $\rho(r)$ for a given quantum state of the atom. We then have

$$\int \rho(r)\, d\tau = Z. \tag{48.1}$$

The potential energy of an electron falling in toward the atom will be denoted by e^2V, so that

$$\nabla^2 V = -4\pi\rho. \tag{48.2}$$

It is, however, formally convenient to regard the nuclear charge as not completely point-shaped, but rather as continuously distributed in the form of a δ-function, $\delta(\mathbf{r}) = \delta(x)\,\delta(y)\,\delta(z)$. This leads to

$$\nabla^2 V = -4\pi\rho', \qquad \rho' = \rho - Z\delta(\mathbf{r}). \tag{48.2a}$$

The wave equation for the electron may then be written

$$\left[\nabla^2 + \frac{8\pi m_0}{h^2}(E - e^2V)\right]\psi = 0 \tag{48.3}$$

and consequently treated as a time-dependent stationary problem. We write for positive energy values of the incident electron,

$$(\nabla^2 + k^2)\psi = \frac{2}{a_0} V\psi, \tag{48.4}$$

and

$$k^2 = \frac{8\pi^2 m_0}{h^2} E, \qquad \frac{2}{a_0} V = \frac{8\pi m_0 e^2}{h^2} V, \qquad a_0 = \frac{h^2}{4\pi^2 m_0 e^2}, \tag{48.4a}$$

where a_0 is the Bohr radius of the hydrogen atom, $k = 2\pi/\lambda$, and p and λ the momentum and de Broglie wavelength of the electron at great distances from the atom. Just as we sometimes refer to $\omega = 2\pi\nu$ as the frequency, we shall call k the wave number of the electron; when it appears as a vector $\mathbf{k}$, it will be referred to as the *wave number vector*.

Our task is now to find solutions of (48.3) which correspond to particular physical scattering problems. Since the positive energy spectrum is continuous, we may regard the energy E—and hence also k—as given. The wave function ψ is interpreted such that $|\psi|^2 = \psi^*\psi$ signifies the number of

electrons per unit volume. Thus, for instance, we would obtain, for $V = 0$, the solution

$$\psi_0 = e^{ikz}, \tag{48.5}$$

of (48.4). This characterizes the state of the electron such that it moves with a uniform rectilinear velocity, and the momentum $p = hk/2\pi$, in the positive z-direction. On the other hand, it yields a spatial density equal to unity; hence it may also be said to represent a homogeneous electron beam with one electron per unit volume.

However, ψ_0 is only an approximate solution of (48.4). Regarding V as a perturbation we may say that ψ_0 is the unperturbed solution. The exact solution of (48.4) also contains additional terms which we might call the perturbed terms of the wave function. It is possible to adjust these in such a way that they represent outgoing spherical waves which attain the asymptotic form

$$\psi_0' = \frac{e^{ikr}}{r} f(\vartheta, \varphi), \tag{48.6}$$

at great distances from the atom; here ϑ is the scattering angle and φ the equatorial angle about the direction of the incident electrons. The quantity

$$\sigma(\vartheta, \varphi) = |f(\vartheta, \varphi)|^2 = r^2 |\psi_0'|^2 \tag{48.7}$$

is called the *differential scattering cross section* and measures the number of scattered electrons per unit solid angle, relative to the number of incident electrons per unit area normal to the electron beam. For a spherically symmetric field $V(r)$, $\sigma(\vartheta, \varphi) = \sigma(\vartheta)$ is a function of the scattering angle only, and $\int \sigma(\vartheta)\, d\Omega$ is the *total scattering cross section.*

Assuming ψ_0' to be small relative to ψ_0, we may with a good approximation replace (48.4) by the equation

$$(\nabla^2 + k^2)\psi_0' = \frac{2}{a_0} V\psi_0; \tag{48.8}$$

this is known as the Born approximation. We shall see later that it is very useful, provided the electron velocities are sufficiently high and the de Broglie wavelengths correspondingly small. Since the right-hand side is a known function, this equation may be solved without difficulty; it may be regarded as the equation for elementary spherical waves emitted from the spatial regions of the atom where the quantity on the right-hand side is different from zero.

Solution of the Perturbation Equation. Outgoing Waves

We assume the solution of (48.8) to be known and write it as

$$\psi_0'(\mathbf{r}) = -\frac{1}{4\pi} \int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \cdot \frac{2}{a_0} V(\mathbf{r}')\psi_0(\mathbf{r}')\, d\tau'. \tag{48.9}$$

For large r we may replace $|\mathbf{r} - \mathbf{r}'|$ by r in the denominator and by $r - \mathbf{n} \cdot \mathbf{r}$ in the exponential function; $\mathbf{n}$ is the unit vector in the direction ϑ, φ. Writing $\mathbf{k}$ for the wave number vector in this direction, and $\mathbf{k}_0$ for the corresponding incident direction, we find that

$$r\psi_0'(\mathbf{r}) = -\frac{2}{a_0}\frac{e^{ikr}}{4\pi}\int e^{i\mathbf{K}\mathbf{r}} V(r)\, d\tau, \qquad \mathbf{K} = \mathbf{k}_0 - \mathbf{k}. \tag{48.10}$$

Using

$$\nabla^2 e^{i\mathbf{K}\mathbf{r}} = -K^2 e^{i\mathbf{K}\mathbf{r}}, \qquad K = |\mathbf{k}_0 - \mathbf{k}| = 2k \sin\frac{\vartheta}{2}, \tag{48.11}$$

and (48.2a), this integral may be rewritten as

$$r\psi_0'(\mathbf{r}) = -\frac{2a_0 e^{ikr}}{(Ka_0)^2}\int e^{i\mathbf{K}\mathbf{r}}\, \rho'(r)\, d\tau. \tag{48.12}$$

Thus we obtain a scattering cross section

$$\sigma(\vartheta) = f^2(\vartheta), \qquad f(\vartheta) = \frac{2a_0}{(Ka_0)^2} F_{nn}(K), \tag{48.13}$$

where

$$F_{nn}(K) = Z - f_{nn}(K), \qquad f_{nn}(K) = \int e^{i\mathbf{K}\mathbf{r}}\, \rho(r)\, d\tau, \tag{48.13a}$$

and $f_{nn}(K)$ is the previously discussed atomic form factor referred to a fixed quantum state Ψ_n for the atom. When $K \to 0$, we have $f_{nn}(K) \to Z$.

There is evidently a considerable similarity between the scattering of rapid electrons and that of short-wave electromagnetic radiation, since both of these phenomena are determined mainly by the same atomic form factor. There is, however, a characteristic difference: that the scattering cross section for electrons is proportional to $1/K^4$ or $1/\sin^4(\vartheta/2)$. For this reason the intensity decreases very rapidly with the scattering angle which may be compared with the scattering of X-rays, even though the factor $|Z - f_{nn}(K)|^2$ acts in the opposite direction.

Scattering from a Model Atom. Rutherford's Formula

We shall consider, as an example, the charge distribution

$$\rho(r) = \frac{1}{4\pi}\frac{Z}{2}\left(\frac{2}{a}\right)^3 e^{-(2/a)r}. \tag{48.14}$$

For $Z = 1$, $a = a_0$, this corresponds to the distribution of charge within the hydrogen atom in the ground state; for $Z = 2$ and $a = \left(\frac{16}{27}\right) a_0$, it corresponds approximately to the ground state of helium. A simple calculation

yields

$$f(K) = \frac{Z}{(1 + s^2)^2}, \qquad s = \frac{1}{2} Ka = ka \sin \frac{\vartheta}{2} \tag{48.15}$$

or

$$F(K) = Z - f(K) = \frac{Z(Ka)^2(\frac{1}{2} + \frac{1}{4}s^2)}{(1 + s^2)^2}. \tag{48.16}$$

Let us assume that the wavelength is not too small or that the scattering angle is not very large, so that s is small. By (48.13) and (48.16) the differential scattering cross section will then be of the order of $\sigma(\vartheta) = Z^2 a_0^2 (a/a_0)^4$. Hence it decreases rapidly with an increasing concentration of the charge surrounding the nucleus. Conversely it will increase strongly with a corresponding dilution of charge, so that one rapidly obtains the scattering that would be produced by a bare atomic nucleus.

For $a \to \infty$, we have $F(K) = Z$. Writing $K = 2k \sin(\vartheta/2)$, $k = (2\pi/h)m_0 v$, the differential scattering cross section is then

$$\sigma(\vartheta) = b_0^2 \Big/ \sin^4\left(\frac{\vartheta}{2}\right), \qquad b_0 = \frac{Z}{2a_0 k^2} = \frac{Ze^2}{2m_0 v^2}, \tag{48.17}$$

in agreement with the Rutherford formula for the scattering of electrons or α-particles by an atomic nucleus.

Problems

1. Calculate the atomic form factor for the charge distribution (48.14).
2. Calculate the differential scattering cross section; show, by integrating over all solid angles $d\Omega = \sin\vartheta \, d\vartheta \, d\varphi$ that the total scattering cross section is

$$\sigma = 4\pi Z^2 \alpha^2 \left(\frac{a}{a_0}\right)^2 \cdot \frac{1 + \frac{3}{2}(ka)^2 + \frac{7}{12}(ka)^4}{[1 + (ka)^2]^3}.$$

3. Calculate the scattering amplitude $f(\vartheta)$ for the electron distribution

$$\rho_i(r) = Z_i^3 \exp\left(\frac{-2Z_i r}{a_0}\right) \pi a_0^3$$

for the individual electrons $i = 1, 2, \cdots, Z$, by means of a successive screening $Z_{i+1} = Z - i$ of the nucleus.

4. Solve the inhomogeneous equation

$$(\nabla^2 + k^2)\psi(\mathbf{r}) = F(\mathbf{r})$$

by means of a method similar to that used in the solution of Poisson's equation: that is, use the auxiliary (Green's) function

$$\frac{\Phi = e^{ik|r-r'|}}{|\mathbf{r} - \mathbf{r}'|.}$$

Show that the solution agrees with (48.9).

5. Show, using Problem 7, that (48.13a) may be written

$$f_{nn}(K) = \int \frac{\sin Kr}{Kr} \rho(r)\, d\tau.$$

6. Let the electron wavelength be $\lambda = a_0$. Calculate the kinetic energy in electron volts. Determine the maximum value of Ka_0 and its value for an energy of 30,000 eV.
7. Put $e^{i\mathbf{Kr}} = e^{iKr\cos\vartheta}$ and $d\Omega = \sin\vartheta\, d\vartheta\, d\varphi$. We want to find the mean value of the exponential function, averaged over all directions, for a fixed length $r = |\mathbf{r}|$. Show that

$$\int e^{i\mathbf{Kr}} \frac{d\Omega}{4\pi} = \frac{\sin Kr}{Kr}.$$

8. Put $\mathbf{k}_0\mathbf{r} = kr\cos\vartheta_0$, $\mathbf{kr} = kr\cos\vartheta$. Show that

$$\cos\vartheta_0 = \cos\vartheta\cos\vartheta + \sin\vartheta\sin\vartheta\cos\Phi,$$

where ϑ is the angle between the two vectors $\mathbf{k}_0$ and $\mathbf{k}$, and Φ the angle between the planes $(\mathbf{k}, \mathbf{k}_0)$ and $(\mathbf{k}, \mathbf{r})$. Put $d\Omega = \sin\vartheta\, d\vartheta\, d\Phi$ and show, using Problem 7, that

$$\int e^{ikr(\cos\vartheta_0 - \cos\vartheta)} \frac{d\Omega}{4\pi} = \frac{\sin Kr}{Kr}.$$

49. THE METHOD OF PARTIAL WAVES

Resolution of the Incident Wave into Partial Spherical Waves

We first define a set of functions $j_l(x)$, $l = 0, 1, 2, \cdots$ by the equation

$$i^l j_l(x) = \frac{1}{2}\int_{-1}^{+1} e^{ix\xi} P_l(\xi)\, d\xi. \tag{49.1}$$

Since $P_l(1) = 1$, $P_l(-1) = i^{2l}$, $j_e(x)$ approaches the asymptotic value

$$j_l(x) \to \frac{e^{ix}i^{-l} - e^{-ix}i^l}{2ix} = \frac{\sin[x - l(\pi/2)]}{x} \tag{49.2}$$

for large x. Conversely it may be shown that

$$e^{ix\xi} = \sum_l (2l + 1) i^l j_l(x) P_l(\xi), \tag{49.3}$$

since the multiplication of this equation by $P_l(\xi)$ and integration yields (49.1) because of the normalization integral for the orthogonal functions $P_l(\xi)$.

It now follows from (49.3) that

$$e^{ikz} = e^{ikr\cos\vartheta} = \sum_l (2l+1) i^l j_l(kr) P_l(\cos\vartheta). \tag{49.4}$$

This is called a resolution into partial spherical waves by means of the spherical functions $P_l(\cos\vartheta)$. The asymptotic form is

$$e^{ikz} = \sum_l (2l+1) \frac{e^{ikr} - e^{-i(kr-l\,)}}{2ikr} P_l(\cos\vartheta). \tag{49.5}$$

Since the incident wave obeys the differential equation

$$(\nabla^2 + k^2) e^{ikz} = 0, \tag{49.6}$$

the functions $j_l(kr)$ must satisfy the equation

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} + k^2\right] j_l(kr) = 0. \tag{49.7}$$

This is closely related to the differential equation for the Bessel functions $J_{l+1/2}(kr)$. Using the asymptotic formulas for the two functions, one finds that

$$j_l(x) = \left(\frac{\pi}{2x}\right)^{1/2} J_{l+1/2}(x), \tag{49.8}$$

$$j_0(x) = \frac{\sin x}{x}, \qquad j_1(x) = -\frac{\cos x}{x} + \frac{\sin x}{x^2}, \qquad \text{etc.}$$

Solution of Wave Equations by Separation. Scattering Phases

In the wave equation (45.4)

$$(\nabla^2 + k^2)\psi = U\psi, \qquad U(r) = \frac{2}{a_H} V(r) \tag{49.9}$$

we substitute

$$\psi = \sum_l (2l+1) i^l e^{i\eta_l} R_l(r) P_l(\cos\vartheta) \tag{49.10}$$

and obtain the equation for the radial functions

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} + k^2\right] R_l(r) = U(r) R_l(r). \tag{49.11}$$

If we require that $R_l(0) = 0$ and that the function be real, it will have an

asymptotic value which we normalize such that

$$R_l(r) \to \frac{\sin\,[kr + \eta_l - l(\pi/2)]}{kr} = \frac{1}{2ikr}\left\{\exp\left[i\left(kr + \eta_l - l\frac{\pi}{2}\right)\right]\right.$$
$$\left. - \exp\left[-i\left(kr + \eta_l - l\frac{\pi}{2}\right)\right]\right\}, \quad (49.12)$$

where the quantities η_l, which will be referred to as scattering phases, must be determined by the solution of (49.11).

Because of the factor $e^{i\eta_l}$ introduced into (49.10), ψ will have the same form as (49.5) with respect to the last term. Hence we may write

$$\psi = \psi_0 + \psi_0', \qquad \psi_0 = e^{ikz}, \quad (49.13)$$

where

$$\psi_0' \to \frac{e^{ikr}}{ir} f(\vartheta), \qquad f(\vartheta) = \frac{1}{k}\sum_l (2l + 1)P_l(\cos\vartheta)e^{i\eta}\,\sin\eta_l \quad (49.14)$$

represents only outgoing spherical waves. The differential scattering cross section is then

$$\sigma(\vartheta) = |r\psi_0'|^2 = |f(\vartheta)|^2, \quad (49.15)$$

and the total scattering cross section

$$\sigma = 2\pi\int_0^\pi \sigma(\vartheta)\sin\vartheta\,d\vartheta = \frac{4\pi}{k^2}\sum_l (2l + 1)\sin^2\eta_l. \quad (49.16)$$

Approximate Determination of the Phase and Comparison with the Born Approximation

Combining (49.7) and (49.11), we may deduce the following equation

$$\frac{d}{dr}\left[r^2\left(j_l\frac{dR_l}{dr} - R_l\frac{dj_l}{dr}\right)\right] = r^2UR_lj_l, \qquad j_l = j_l(kr). \quad (49.17)$$

From this it follows by integration and use of the asymptotic expressions (49.2) and (49.12) that

$$\frac{\sin\eta_l}{k} = -\int_0^\infty U(r)R_l(r)j_l(kr)r^2\,dr. \quad (49.18)$$

When $\sin\eta_l/k$ is sufficiently small, $R_l(r)$ will differ very little from $j_l(kr)$; we may, to a good approximation, replace (49.18) by

$$\frac{\sin\eta_l}{k} = -\int_0^\infty U(r)j_l^2(kr)r^2\,dr. \quad (49.19)$$

Substituting this in the expression (49.14) for the scattering amplitude

$f(\vartheta)$ and writing (to the same approximation) $e^{i\eta_l} = 1$, we find

$$f(\vartheta) = -\int_0^\infty U(r)\left[\sum_l (2l+1)P_l(\cos\vartheta)j_l^2(kr)\right]r^2\,dr. \tag{49.20}$$

By a well-known expansion theorem from the theory of Bessel functions we have

$$\frac{\sin Kr}{Kr} = \sum_l (2l+1)P_l(\cos\vartheta)j_l^2(kr), \tag{49.21}$$

since

$$K = 2k\sin\frac{\vartheta}{2}.$$

Substitution in (49.20) then yields

$$f(\vartheta) = -\int_0^\infty U(r)\frac{\sin Kr}{Kr}r^2\,dr, \tag{49.22}$$

an equation that is also obtainable from (45.6) and (45.10).

Problems

1. Use the results of Problem 8 in Section 48, and the expansion (49.4), to show that

$$e^{i\mathbf{Kr}} = e^{ikr(\cos\vartheta_0-\cos\vartheta)} = \sum_{ll'}(2l+1)(2l'+1)i^{l-l'}P_l(\cos\vartheta_0)P_l(\cos\vartheta)j_l(kr)j_{l'}(kr).$$

2. Use the expansion $P_l(\cos\vartheta_0) = P_l(\cos\vartheta)P_l(\cos\vartheta)$ + (terms containing $\cos m\Phi$), and average over all directions of $\mathbf{r}$ (or all values of ϑ and Φ in $d\Omega = \vartheta\,d\vartheta\,d\Phi$ to prove that (49.21) is valid.

50. SCATTERING OF RAPID ELECTRONS IN A REAL ATOM

Elastic or Coherent Scattering

As we have seen, the scattering of electromagnetic waves and electrons in an atom show many similar features; this applies, in particular, to rapid electrons and short-wave radiation such as X-rays. For slow electrons, however, serious complications appear. One of these is that it is, in principle, not possible to distinguish sharply between incident and atomic electrons; hence we must account for the exchange of electrons between the incident beam and the atoms. This is, however, not the greatest of our troubles. It turns out that certain resonance effects occur that have no parallel in the atom–photon interaction. Several of these effects have not up to now been given a satisfactory treatment, except by means of the method of partial

waves; even then the discussion is very difficult. It appears to be impossible to find a simple law for the scattering of electrons moving with any velocity, analogous to the dispersion formula for electromagnetic radiation, that is valid for all frequencies. Hence we must abandon the attempt to give completely parallel treatments of the scattering of electrons and radiation. Because of the formal complexity and involved calculations encountered in this topic, we shall (somewhat reluctantly) restrict ourselves to the treatment of rapid electrons, where the Born approximation may still be applied.

On the other hand, the treatment of incoherent or inelastic scattering of electrons presents no difficulty. This is connected with the fact that the incident electrons may be described by a quantum-mechanical law, that is, the Schrödinger wave equation, while light waves have hitherto been treated in a semiclassical fashion, using Maxwell's equations.

The physical problem of the greatest practical interest is to determine the scattering from atoms in the ground state, which is usually a spherically symmetric S-state; for simplicity we assume in the present discussion that this is always the case. Moreover no particular difficulties appear in the treatment of atoms with any number of orbital electrons, as long as the incident electrons are rapid; hence we consider an atom with Z electrons and the nuclear charge Ze.

To simplify the notation we write $\Phi = \psi\Psi$ for the wave function; ψ then refers to the incident and scattered electrons, while Ψ denotes the eigenfunctions of the atom. The potential energies of the atomic and incident electrons are denoted by e^2V and e^2V', respectively, so that

$$\begin{aligned} V &= -\sum_{i=1}^{Z}\frac{Z}{r_i} + \sum_{i>k}\frac{1}{r_{ik}}, \\ V' &= -\frac{Z}{r_e} + \sum_{i=1}^{Z}\frac{1}{r_{ie}}, \end{aligned} \tag{50.1}$$

where e refers to the outer electron. Moreover we write ∇^2 for the sum of the Laplacian operators of the atomic electrons, and correspondingly ∇_e^2 for the outer electron. Finally we write the energy E_e of the atom as $(h^2/8\pi^2m_0)\varepsilon$. The wave equation for the entire system will then read

$$\left(\nabla_e^2 + \nabla^2 + k^2 + \varepsilon - \frac{2}{a_0}V\right)\Phi = \frac{2}{a_0}V'\Phi. \tag{50.2}$$

We now assume that the atomic eigenfunction in the ground state (or any other S-state) Ψ_n is known and normalized,

$$\left(\nabla^2 + \varepsilon_n - \frac{2}{a_0}V\right)\Psi_n = 0, \qquad \int \Psi_n^*\Psi_n\, d\tau = 1, \quad d\tau = d\tau_1 \cdots d\tau_Z. \tag{50.3}$$

As a first approximation we substitute $\Phi = \psi\Psi_n$ in (50.2), multiply by Ψ_n^* and integrate, thus obtaining

$$(\nabla_e^2 + k^2)\psi = U(\mathbf{r}_e)\psi, \qquad U(\mathbf{r}_e) = \frac{2}{a_0}\int \Psi_n^* V' \Psi_n \, d\tau. \tag{50.4}$$

For the statistical spatial distribution of the ith electron we write

$$\rho_i(\mathbf{r}_i) = \int \Psi_n^* \Psi_n \frac{d\tau}{d\tau_i}, \qquad \int \rho_i(\mathbf{r}_i)\, d\tau_i = 1 \tag{50.5}$$

which leads to

$$\begin{aligned} U(\mathbf{r}_e) &= \frac{2}{a_0}\left[\int \frac{\rho(r)\, d\tau}{|\mathbf{r}_e - \mathbf{r}|} - \frac{Z}{r_e}\right], \\ \rho(r) &= \sum_i \rho_i(\mathbf{r}), \qquad \int \rho(r)\, d\tau = Z. \end{aligned} \tag{50.6}$$

Here $d\tau$ refers to the coordinate space of a single electron. For $U(\mathbf{r}_e)$ we then have the equation

$$\nabla_e^2 U = -\frac{2}{a_0} 4\pi[\rho(r_e) - Z\,\delta(\mathbf{r}_e)]. \tag{50.7}$$

The subsequent treatment runs along exactly the same lines as that of (45.7) to (45.13); hence we only state the final result, corresponding to (45.13) and (45.13*a*),

$$\begin{aligned} &\sigma(\vartheta) = f^2(\vartheta), \qquad f(\vartheta) = \frac{2a_0}{(Ka_0)^2}\,[Z - f_{vv}(K)], \\ &f_{nn}(K) = \int e^{i\mathbf{K}\mathbf{r}}\rho(r)\, d\tau = \int \sum_i e^{i\mathbf{K}\mathbf{r}_i}\rho_i(\mathbf{r}_i)\, d\tau_i = \int \sum_i e^{i\mathbf{K}\mathbf{r}_i}\Psi_n^*\Psi_n \, d\tau. \end{aligned} \tag{50.8}$$

Writing, for brevity, the atomic form factor $f_{nn}(K)$ as $f(K)$, we find that formally $f(K) = f_1(K) + \cdots + f_Z(K)$; such an expression may also be obtained by writing Ψ_n as a product of individual functions. However, a much better approximation results if we antisymmetrize this product in the two groups of electrons with the same spin. This leads to a wave function in the form of a product of two determinants. Hence the contributions to $f(K)$ from electrons with the same spin must be equal. If the atom contains an even number of electrons, half of which are distributed on each of the two spin directions, each electron will then furnish the same contribution

$$f_{nn}(K) = Z\int e^{i\mathbf{K}\mathbf{r}_i}\rho_i(\mathbf{r}_i)\, d\tau_i = Z\int e^{i\mathbf{K}\mathbf{r}_i}\Psi_n^*\Psi_n \, d\tau, \tag{50.8a}$$

where $\mathbf{r}_i$ now denotes the position vector of any one of the electrons.

Inelastic or Incoherent Scattering

We now assume that all atomic eigenfunctions are known and that the total wave function [the solution of (50.2)] may be written as

$$\Phi = \sum_n \psi_n \Psi_n, \qquad \int \Psi_m^* \Psi_n \, d\tau = \delta_{mn}, \tag{50.9}$$

to a fair approximation; n here denotes the aggregate of all (open and closed) atomic states, together with $3Z$ different quantum numbers. The detailed treatment is therefore somewhat involved; however, it is the principle of the matter that primarily concerns us here, that is, how to calculate the cross section of inelastic scattering for the quantum transition $n \to m$ in the atom. Writing

$$k_m^2 = k^2 + \varepsilon_n - \varepsilon_m \tag{50.10}$$

and substituting (50.9) in (50.2), multiplying by Ψ_m^* and integrating, we obtain

$$(\nabla_e^2 + k_m^2)\psi_m = U_{mn}\psi_n, \qquad U_{mn} = \frac{2}{a_0}\int \Psi_m^* V' \Psi_n \, d\tau. \tag{50.11}$$

Here we have ignored—since they are usually very small—all terms on the right-hand side, except the one arising from Ψ_n.

Evidently we have to solve equations of the same type as those previously discussed. We obtain the differential scattering cross sections

$$\sigma_{mn}(\vartheta) = \frac{k_m}{k} |f_{mn}(\vartheta)|^2 \tag{50.12}$$

for each quantum transition $n \to m$, where $f_{mn}(\vartheta)$ is the scattering amplitude. The factor k_m/k is due to the change in the velocity or momentum of the electrons by (50.10). The scattering amplitude is now

$$f_{mn}(\vartheta) = -\frac{2a_0}{(Ka_0)^2} f_{mn}(K), \qquad f_{mn}(K) = \int \sum_i e^{i\mathbf{K}\mathbf{r}_i} \Psi_m^* \Psi_n \, d\tau, \tag{50.13}$$

$$\mathbf{K} = \mathbf{k} - \mathbf{k}_m, \qquad K = |\mathbf{k} - \mathbf{k}_m|.$$

Actually the formula for $f_{mn}(K)$ appears, just as for the elastic scattering, as an integral

$$f_{mn}(K) = \int e^{\mathbf{K}\mathbf{r}} \sum_i \rho_i(\mathbf{r}) \, d\tau, \qquad \rho_i(\mathbf{r}_i) = \int \Psi_m^* \Psi_n \frac{d\tau}{d\tau_i} \tag{50.14}$$

over a sum of electron charges, in this case combination charges. If $\mathbf{r}$ and $d\tau$ in the first integral are formally replaced by $\mathbf{r}_i$ and $d\tau_i$, and the summation sign moved, (50.13) results. The atomic nucleus does not contribute to the inelastic scattering.

Sum Rule for Coherent and Incoherent Scattering

For scattering from a one-electron atom the rules of matrix multiplication and (50.13) lead to

$$\sum_m |f_{mn}(K)|^2 = \sum_m (e^{-i\mathbf{Kr}})_{nm}(e^{i\mathbf{Kr}})_{mn} = (e^{-i\mathbf{Kr}+i\mathbf{Kr}})_{nn} = 1, \qquad (50.15)$$

provided that the energy of the electron is large, relative to the energy transitions in the atom; this is because we may, for the most important transitions, write $k_m = k$ and replace

$$K^2 = k^2 + k_m{}^2 - 2kk_m \cos\vartheta \qquad \text{by} \qquad K = 2k \sin\frac{\vartheta}{2}, \qquad (50.16)$$

that is, by a quantity that is independent of m.

For several electrons the matter is apparently more complicated than in (50.15), since we must now deal with the matrix elements for sums of exponential functions [compare (50.14)]. For incoherent scattering, however, we shall again have two groups of electrons with the same spin. Since the atomic eigenfunction is antisymmetric in pairs of electrons within each of these groups, an interchange of i and k within such a group will lead to an interchange of the exponential functions, while $\Psi_m^*\Psi_n$ remains unaltered. For two equally numerous groups of electrons the interchange of exponential functions from one group to another will also leave the integrals unaltered. Hence we may here also write

$$f_{mn}(K) = Z\int e^{i\mathbf{Kr}_i}\Psi_m^*\Psi_n \, d\tau, \qquad (50.17)$$

where i represents any one of the electrons.

Under the same assumptions as in (50.16) we therefore arrive at a result similar to (50.15),

$$\sum_m |f_{mn}(K)|^2 = Z^2, \qquad (50.18)$$

for atoms with several electrons. Thus, writing $F_{nn}(K) = Z - f_{nn}(K)$, $F_{mn}(K) = -f_{mn}(K)$, we obtain the following rule for the sum of elastic and inelastic (or coherent and incoherent) electron scattering

$$\sum_m |F_{mn}(K)|^2 = [Z - f_{nn}(K)]^2 + Z^2 - f_{nn}{}^2(K). \qquad (50.19)$$

The first term represents the coherent scattering by the nucleus and atomic electrons; the last term represents the total incoherent scattering which is exclusively due to the electrons. When $K = 2k \sin\vartheta/2 \to 0$, both the coherent and incoherent parts vanish. This means that the atomic electrons and the nucleus will mutually screen each other off, with respect to slowly moving

electrons. This result is of limited validity, however, since we have assumed above that the electrons move fairly rapidly and have not considered any of the several interesting physical effects appearing in the scattering of slow electrons.

Problems

1. Assume that $Z = 2N$ and that the atomic eigenfunctions may be approximately expressed as a product of two determinants, defined by means of the same set of orthonormal functions $\Phi_1, \Phi_2, \cdots, \Phi_N$, as follows:

$$\Psi = \frac{1}{N!} \begin{vmatrix} \Phi_1(1) \cdots \Phi_1(N) \\ \cdots \\ \Phi_N(1) \cdots \Phi_N(N) \end{vmatrix} \cdot \begin{vmatrix} \Phi_1(N+1) \cdots \Phi_1(2N) \\ \cdots \\ \Phi_N(N+1) \cdots \Phi_N(2N) \end{vmatrix}$$

Show that $\int \Psi^* \Psi \, d\tau_1 \cdots d\tau_N = I^2$,

$$I = \int \begin{vmatrix} \Phi_1(1) \cdots \Phi_1(N) \\ \cdots \\ \Phi_N(1) \cdots \Phi_N(N) \end{vmatrix} \Phi^*(1) \cdots \Phi_N^*(N) \, d\tau_1 \cdots d\tau_N$$

$$= \int \begin{vmatrix} \Phi_1^*(1)\Phi_1(1) \cdots \Phi_N^*(N)\Phi_1(N) \\ \cdots \\ \Phi_1^*(1)\Phi_N(1) \cdots \Phi_N^*(N)\Phi_N(N) \end{vmatrix} d\tau_1 \cdots d\tau_N,$$

and that this integral is equal to unity.

2. Show, by interchanging i and k, that

$$g_i(K) = \int e^{i\mathbf{K}\mathbf{r}_i} \Psi^* \Psi \, d\tau = \int e^{i\mathbf{K}\mathbf{r}_k} \Psi^* \Psi \, d\tau = g_k(K),$$

and consequently, using (50.8), that

$$f_{nn}(K) = Z \int e^{i\mathbf{K}\mathbf{r}_i} \Psi^* \Psi \, d\tau = Z g(K).$$

Furthermore show (by coordinate interchanges) that

$$N g(K) = \sum_i g_i(K).$$

where

$$g_i(K) = \int \begin{vmatrix} \Phi_1^*(1)\Phi_1(1) \cdots \Phi_N^*(N)\Phi_1(N) \\ \Phi_1^*(1)\Phi_N(1) \cdots \Phi_N^*(N)\Phi_N(N) \end{vmatrix} e^{i\mathbf{K}\mathbf{r}_i} \, d\tau_1 \cdots d\tau_N.$$

51. DETERMINATION OF QUANTUM TRANSITIONS BY TIME-INDEPENDENT PERTURBATIONS

Stationary Systems as Time-Dependent Problems

In our discussion of electron scattering we regarded the atom and electron as a system in a stationary state, characterized by an incident plane wave and an outgoing spherical wave. The problem may, however, be attacked from a very different angle. Disregarding the interaction between the electron and the atom, we may determine several different solutions for the same total energy. For instance, we may consider a solution where the atom is in the ground state, while the electron is in states corresponding to one plane wave in the direction $\mathbf{n}_0$ and another in the direction $\mathbf{n}$. Let us assume that at the time $t = 0$ only the first obtains. If we now take the interaction into account, the wave in the direction $\mathbf{n}$ will have attained a certain strength at a later time t; if this strength is proportional to t, the factor of proportionality will furnish us with a measure of the transition probability for this elastic or coherent scattering process.

Similarly we may consider a state where the atom has been excited, while the scattered wave corresponds to an electron with a lower energy, so that the total energy is constant in this case also. By determining how this wave increases with time we obtain an expression for the strength of the inelastic or incoherent electron scattering. Since the method employed in the calculation of the time-dependent coefficients of expansion is one of approximation the result will of course also be only approximately correct. It turns out that this method corresponds, more or less, to the Born approximation.

Since it is just this method that is used in quantum electrodynamics to calculate the interaction between the electrons and the radiation field, we shall discuss its theoretical background in some detail.

Perturbation by Time-Independent Interactions

Let us consider a time-independent perturbation H', which we assume begins to operate at $t = 0$. Whether it has, in fact, acted on the system before this time is irrelevant for us, provided that we know for certain the initial state at $t = 0$, say $\psi = \psi_n$. We may then immediately apply the equation (42.8), which we write as

$$\begin{aligned} c_m &= -\frac{2\pi i}{h}\int_0^t H'_{mn}\exp\left[\frac{2\pi i}{h}(E_m - E_n)t\right]dt \\ &= \frac{H'_{mn}}{E_m - E_n}\left\{1 - \exp\left[\frac{2\pi i}{h}(E_m - E_n)t\right]\right\}, \end{aligned} \tag{51.1}$$

since H'_{mn} is time-independent.

If we had $E_m = E_n$ exactly, c_m would be proportional to t and $|c_m|^2$ to t^2; hence no time-independent transition probability would result. However, we are not interested in finding the number of transitions with the exact final value $E_m - E_n$, since—as is well-known—there will always be some uncertainty in the energy for finite intervals of time. Our primary objective is to determine the transition to energy states around $E_m - E_n$; these have an approximately continuous distribution with, say, $N_m(E_m)\,dE_m$ states in the interval dE_m. The function $N_m(E_m)$ has the dimension of a reciprocal energy.

From (51.1) we find, as an expression for the strength of the state ψ_m,

$$|c_m|^2 = \frac{2\,|H'_{mn}|^2}{(E_m - E_n)^2} \cdot \left[1 - \cos\frac{2\pi}{h}(E_m - E_n)t\right]. \tag{51.2}$$

With the new variable $x = 2\pi/h(E_m - E_n)t$ (which may, for large t, be taken to have the limits $\pm\infty$, without noticeable error), we obtain

$$\int |c_m|^2\, N(E_m)\, dE_m = \frac{4\pi^2}{h} N_m(E_n)\, |H'_{mn}|^2\, t. \tag{51.3}$$

The transition probability, or the number of quantum jumps per unit time, hence becomes

$$w_{mn} = \frac{4\pi^2}{h} N_m(E_n)\, |H'_{mn}|^2 \tag{51.4}$$

for a single system in the state ψ_n; this quantity has the dimension of a reciprocal time, or frequency.

Intermediate States

If $H'_{mn} = 0$, no quantum transition between ψ_n and ψ_m may occur, by (51.4). This result rests, however, on an approximation that is too rough; actually the system may pass through intermediate states ψ_i, provided both H'_{mi} and H'_{in} are different from zero.

To see this we consider the equations

$$\begin{aligned} \dot{c}_i &= -\frac{2\pi i}{h} H'_{in} \exp\left[\frac{2\pi i}{h}(E_i - E_n)t\right] c_n, \\ \dot{c}_m &= -\frac{2\pi i}{h} \sum_i H'_{mi} \exp\left[\frac{2\pi i}{h}(E_m - E_i)t\right] c_i. \end{aligned} \tag{51.5}$$

It should be noted that the energy law need not hold for the intermediate states. We have then $E_i \neq E_n$ and $E_m \neq E_i$, but $E_m \approx E_n$. The solution for c_i, when $c_n(0) = 1$, is given by (51.1) if we replace m by i. Further integration

leads to

$$c_m = \sum_i \frac{H'_{mi}H'_{in}}{E_i - E_n}\left[\frac{1 - \cos\frac{2\pi}{h}(E_m - E_i)t}{E_m - E_i} - \frac{1 - \cos\frac{2\pi}{h}(E_m - E_n)t}{E_m - E_n}\right]. \tag{51.6}$$

In the calculation of the transition probability it turns out that we may ignore the first term; the final result is then

$$w_{mn} = \frac{4\pi^2}{h} N_m(E_n)\left|\sum_i \frac{H'_{mi}H'_{in}}{E_i - E_n}\right|^2. \tag{51.7}$$

It is evident from (51.7) how the transition probability is determined by the matrix elements for both direct transitions and transitions through intermediate states.

Application to Electron Scattering

We shall apply the theory to electron scattering in an atom with known electron states Ψ_n. The incident electron beam is characterized by the plane wave $\Phi_n = e^{i\mathbf{k}_n\mathbf{r}}$. We shall now investigate the probability that the system passes over into a state Ψ_m for the atom and a wave with the wave number vector $\mathbf{k}_m$ for the electron, $\Phi_m = e^{i\mathbf{k}_m\mathbf{r}}$. Thus we put

$$\begin{aligned} \Psi_n &= \Phi_n\Psi_n, \qquad \Psi_m = \Phi_m\Psi_m, \\ k_m^2 &= k_n^2 - \frac{8\pi^2 m_0}{h^2}(E_m - E_n), \end{aligned} \tag{51.8}$$

so that the energy of the total (atom + electron) system is unchanged.

The interaction is here

$$H' = \sum_i \frac{e^2}{r_{ei}} - \frac{Ze^2}{r_e}, \tag{51.9}$$

where the incident electron has been indexed by e, and the atomic electrons by $i = 1, 2, \cdots, Z$. Since $\int \Psi_m^*\Psi_n\, d\tau = 0$, the last term is of no importance for inelastic scattering.

Writing (as before) $\mathbf{K} = \mathbf{k}_n - \mathbf{k}_m$, and also for brevity,

$$U_i(\mathbf{r}_e) = \int \frac{\Psi_m^*\Psi_n}{r_{ei}}\, d\tau_A, \tag{51.10}$$

we obtain

$$H'_{mn} = e^2\int e^{i\mathbf{K}\mathbf{r}} \sum_i U_i(\mathbf{r})\, d\tau. \tag{51.11}$$

Thus H'_{mn}—like $f_{mn}(K)$ in (47.13)—becomes a function of $K = |\mathbf{k}_n - \mathbf{k}_m|$.

The function $U_i(\mathbf{r})$ in (51.11) is a potential function that represents the potential energy between the ith atomic electron and the incident electron. This function satisfies Poisson's equation

$$\nabla^2 U_i(\mathbf{r}) = -4\pi\rho_i(\mathbf{r}), \tag{51.12}$$

where $\rho_i(\mathbf{r})$ is the density function for the ith atomic electron

$$\rho_i(\mathbf{r}_i) = \int \Psi_m^* \Psi_n \frac{d\tau_A}{d\tau_i}. \tag{51.13}$$

Since $e^{i\mathbf{Kr}}$ satisfies the equation $e^{i\mathbf{Kr}} = -\nabla^2 e^{i\mathbf{Kr}}/K^2$, we may rewrite (51.11) as

$$H'_{mn} = \frac{4\pi e^2}{K^2} f_{mn}(K), \qquad f_{mn}(K) = \int e^{i\mathbf{Kr}} \sum_i \rho_i(\mathbf{r})\, d\tau, \tag{51.14}$$

using Green's or Gauss' integral theorem and (51.12). The last quantity may by means of (51.13) be written

$$f_{mn}(K) = \int \sum_i e^{i\mathbf{Kr}_i} \rho_i(\mathbf{r}_i)\, d\tau_i = \int \sum_i e^{i\mathbf{Kr}_i} \Psi_m^* \Psi_n\, d\tau_A. \tag{51.15}$$

Hence $f_{mn}(K)$ is by (47.14) the same as our previously discussed atomic form factor for combination charges in the atom, with respect to the quantum transition $n \to m$. For an elastic scattering we should have arrived at a slightly different factor, namely, $f_{mn}(K) - Z$, since the last term in (51.9) would then have contributed to the perturbation.

Using (51.4) and (51.14), we thus finally obtain

$$w_{mn} = \frac{64\pi^4 e^4}{h} N_m(E_n) \frac{|f_{mn}(K)|^2}{K^4}. \tag{51.16}$$

The task remaining is now to decide on the physical significance of the quantity $N_m(E_n)$.

If the system is thought of as enclosed in a fixed volume V, the number of energy states in an interval dE_m will be proportional to V. With the normalization, $\Phi = e^{ik_n r}$ however, the number of incident particles will also be proportional to V; more precisely, it will be equal to Vv_0, where $v_0 = P_0/m_0$ is the velocity of the incident electrons. Hence by division with Vv_0, the volume V cancels out, and we may (for simplicity) put $V = 1$. Thus it only remains to divide by v_0.

For a unit volume the number of quantum states within a momentum interval dp (or energy interval $dE = \frac{1}{m_0} p\, dp$) and a solid angle $d\Omega$ is given by

$$N_m(E)\, dE = \frac{p^2\, dp\, d\Omega}{h^3 v_0} = \frac{p}{p_0} \frac{m_0^2}{h^3} d\Omega\, dE. \tag{51.17}$$

Because of this normalization we may identify the transition probability w_{mn} with $\sigma(\vartheta)\, d\Omega$, where $\sigma(\vartheta)$ is the differential scattering cross section. Writing

$$\frac{16\pi^4 e^4}{h^4} = \frac{1}{{a_0}^2}, \qquad \frac{p}{p_0} = \frac{k_m}{k_n},$$

we thus obtain

$$\sigma(\vartheta) = \frac{4}{{a_0}^2} \cdot \frac{k_m}{k_n} \frac{|f_{mn}(K)|^2}{K^2} \tag{51.18}$$

in agreement with previous results.

Problems

1. Calculate the differential and total elastic scattering cross sections for the states $2s$ and $2p$ of the hydrogen atom.
2. Calculate the corresponding inelastic scattering cross sections for the quantum transitions $1s \rightarrow 2s$ and $1s \rightarrow 2p$.

52. THE QUANTUM-ELECTRODYNAMIC TREATMENT OF ELECTROMAGNETIC RADIATION PROBLEMS

A Light Wave as a Particle Beam

The preceding semiclassical treatment of electromagnetic radiation processes is, for several reasons, somewhat less than satisfactory. This applies, above all, to the problem of spontaneous and induced emission, and also to that of incoherent scattering. The latter presents a particularly conspicuous case, when we compare it with the corresponding treatment of electron scattering. Here we are faced with a stationary problem (constant energy) for two interacting quantum-mechanical systems; while, on the other hand, the corresponding treatment of a classical electromagnetic radiation field interacting with a quantum-mechanical system appears as a complicated time-dependent problem (change of the energy of the system due to absorption or emission of radiation). In particular it turns to be impossible to give a satisfactory formal justification for the scattering formula for incoherent radiation. This is, of course, only to be expected in view of the well-known difficulties posed by the problem of emission. A supplementation of the current matrix by off-diagonal terms, representing the incoherent radiation (just as the diagonal terms represent the coherent part), seems to be a plausible way to proceed; nevertheless it is still supported by purely intuitive arguments only.

In view of the fact that the off-diagonal elements appeared in an entirely unforced manner in the analogous treatment of electron scattering, it seems

natural to expect that the above difficulties will vanish if the components of radiation—that is, the photons—are regarded as quantum-mechanical systems. In this case they must be describable in statistical terms by means of some wave equation.

Now it would appear that we already have such an equation, the wave equation for electromagnetic quantities

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\psi = 0. \tag{52.1}$$

A solution of this is

$$\psi = e^{i\mathbf{k}\mathbf{r}-i\omega t}, \qquad k = |\mathbf{k}| = \frac{\omega}{c} = \frac{2\pi}{\lambda}. \tag{52.2}$$

Applying the operator $E = -\dfrac{h}{2\pi i}\cdot\dfrac{\partial}{\partial t}$ to this solution, we obtain $E = h\nu$, that is, the energy of the photon, while the corresponding application of the operator $\mathbf{p} = (h/2\pi i)\,\nabla$ yields $\mathbf{p} = (h/2\pi)\mathbf{k} = (h/\lambda)\mathbf{n} = (h\nu/c)\mathbf{n}$. Hence we may apparently employ the same operator symbolism as for electrons; thus, using (52.1), we may establish a quantum-mechanical energy equation. However, multiplication by $(ch/2\pi i)^2$ leads to an equation of the form

$$H^2\psi = E^2\psi, \qquad H^2 = c^2p^2. \tag{52.3}$$

Just as before, the problem of determining the correct Hamiltonian remains. A resolution of H in terms of anticommutative operators, $H = c(\alpha_1 p_x + \alpha_2 p_y + \alpha_3 p_z)$, might now seem to be an obvious procedure; however, this leads u avoidably to a half-integral spin for the photons, just as for the Dirac electrons. This is known to be incorrect, since photons have an integral spin.

Another possible method of resolving the problem would be to consider the first-order Maxwell equations

$$c\ \mathrm{curl}\ \mathbf{H} = \frac{\partial \mathbf{E}}{\partial t}, \qquad c\ \mathrm{curl}\ \mathbf{E} = -\frac{\partial \mathbf{H}}{\partial t}; \tag{52.4}$$

riting $\psi = \mathbf{E} + i\mathbf{H}$, these may be written formally as

$$c\ \mathrm{curl}\ \psi = i\frac{\partial \psi}{\partial t} \qquad \text{or} \qquad \frac{c}{2\pi}\ \mathrm{curl}\ \psi = -\frac{h}{2\pi i}\frac{\partial \psi}{\partial t}. \tag{52.5}$$

Thus we might put $H = c/2\pi$ curl which would, when applied to divergence-free vectors, yield H^2, in agreement with (52.3). However, ψ would then have a character very different from that of the wave function for electrons: it would be vectorial or—if we like—contain at least two components corresponding, say, to fixed directions of polarization.

Altogether, then, such considerations will lead us into serious difficulties of principle; hence we shall proceed in the usual way and try to describe the electromagnetic field by means of quasimechanical dynamical variables.

Classical Lagrangian and Hamiltonian for the Electromagnetic Field

The electrodynamic equations may, in charge-free space, be written

$$\begin{aligned} &\operatorname{div}\mathbf{E} = 0, && \operatorname{div}\mathbf{H} = 0, \\ &\operatorname{curl}\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{H}}{\partial t}, && \operatorname{curl}\mathbf{H} = \frac{1}{c}\frac{\partial \mathbf{E}}{\partial t}. \end{aligned} \tag{52.6}$$

These are always satisfied by

$$\begin{aligned} &\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, && \mathbf{H} = \operatorname{curl}\mathbf{A}, \\ &\operatorname{div}\mathbf{A} = 0, && \left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{A} = 0. \end{aligned} \tag{52.7}$$

It is easily shown that these equations are derivable from an integral principle (Hamilton's principle) by means of a Lagrangian or Hamiltonian function. The former,

$$L = \frac{1}{8\pi}(\mathbf{E}^2 - \mathbf{H}^2) = \frac{1}{8\pi}\left[\left(\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}\right)^2 - (\operatorname{curl}\mathbf{A})^2\right], \tag{52.8}$$

is a quadratic function in the partial derivatives of the vector potential $\mathbf{A}$, which in turn is a function of the four variables x, y, z, t.

Utilizing the definition of a momentum vector as the canonical conjugate to $\mathbf{A}$,

$$\mathbf{P} = \frac{\partial L}{\partial \dot{\mathbf{A}}} = \frac{1}{4\pi c^2}\frac{\partial \mathbf{A}}{\partial t} = -\frac{1}{4\pi c}\mathbf{E}, \tag{52.9}$$

the Hamiltonian may be written

$$H = \frac{1}{8\pi}(\mathbf{E}^2 + \mathbf{H}^2) = \frac{1}{8\pi}[(4\pi c\mathbf{P})^2 + (\operatorname{curl}\mathbf{A})^2]. \tag{52.10}$$

By means of these functions the field equations may be written in the form of Lagrange's or Hamilton's equations. The Hamiltonian (52.10) is chosen such that it corresponds to the density of field energy.

Resolution into Partial Oscillations. The Quantization of the Field Energy

The preceding formulation was given for purposes of comparison only; and we now proceed to employ directly the electrodynamic equations (52.6)

and (52.7). The method is to resolve the electromagnetic field by means of Fourier analysis into partial oscillations, corresponding to the eigenvibrations for a cavity. The amplitude of these oscillations, which appear as normal coordinates, may then be regarded as dynamical variables for the field and quantized by means of the general rules of quantum mechanics.

Concerning boundary conditions and eigenfunctions for the electromagnetic cavity, we have a fairly free choice, since our only purpose is to obtain a provisional discrete set of normal coordinates for the field. We shall choose the general form

$$\psi = e^{i\mathbf{kr}}. \tag{52.11}$$

In an infinite space, the wave number vector $\mathbf{k}$ will vary over a three-dimensional continuum; while, for a finite cubical volume with the side a, it will range over the points of a cubical lattice with the edge $2\pi/a$. Indexing (as a formal device) the various wave number vectors by s, that is, $\mathbf{k} = \mathbf{k}_s$, and so forth, we obtain the orthonormality relation

$$\int \psi_{s'}^* \psi_s \, d\tau = a^3 \, \delta_{ss'}. \tag{52.12}$$

In this cavity we may now have standing electromagnetic waves of the form

$$\begin{aligned}
\mathbf{A} &= c\sqrt{4\pi}\,\mathbf{e}[e^{i\mathbf{kr}}q(t) + e^{-i\mathbf{kr}}\bar{q}(t)], \\
\mathbf{E} &= -\sqrt{4\pi}\,\mathbf{e}[e^{i\mathbf{kr}}\dot{q}(t) + e^{-i\mathbf{kr}}\dot{\bar{q}}(t)], \\
\mathbf{H} &= ic\sqrt{4\pi}\,(\mathbf{k}\times\mathbf{e})[e^{i\mathbf{kr}}q(t) - e^{-i\mathbf{kr}}\bar{q}(t)], \\
k &= |\mathbf{k}| = \frac{\omega}{c}.
\end{aligned} \tag{52.13}$$

As usual, $\mathbf{e}$ is the polarization vector, $\mathbf{e}^2 = 1$, $\mathbf{e}\cdot\mathbf{k} = 0$; and the entire field appears as a superposition of such waves with different $\mathbf{e}_s$ and $\mathbf{k}_s$. With the chosen normalization we have the energy density

$$W = \frac{1}{a^3}\int \frac{1}{8\pi}(\mathbf{E}^2 + \mathbf{H}^2)\, d\tau = \dot{\bar{q}}\dot{q} + \omega^2\bar{q}q \tag{52.14}$$

or, actually, a sum $W = \sum_s W_s$ of such expressions with the indexed amplitudes q_s and $\bar{q}_s$.

Assuming that we may write

$$\dot{q} = -i\omega q, \qquad \dot{q} = i\omega\bar{q}, \tag{52.15}$$

corresponding to progressive waves in (52.13), we obtain

$$W = 2\omega^2\bar{q}q, \tag{52.16}$$

or strictly speaking,

$$W = \omega^2(\bar{q}q + q\bar{q}). \tag{52.16a}$$

The form (52.16) may be employed as a Hamiltonian if we regard q and $\bar{q}_n$ as noncommuting operators. Thus, for instance, we find

$$\begin{aligned} \dot{p} &= -\frac{\partial W}{\partial q} = -2\omega^2 \bar{q} = 2i\omega \dot{\bar{q}}, \\ p &= 2i\omega \bar{q}, \qquad \bar{p} = -2i\omega q. \end{aligned} \tag{52.17}$$

Hence it follows that the commutation rule $pq - qp = h/2\pi i$ leads to

$$q\bar{q} - \bar{q}q = \frac{h}{4\pi\omega}. \tag{52.18}$$

This relation is easily found to imply, in turn, that

$$Wq - qW = -hvq, \tag{52.19}$$

or by application to an energy eigenstate Φ_N for the oscillator,

$$Wq\Phi_N = q(W - hv)\Phi_N = (W_N - hv)q\Phi_N. \tag{52.20}$$

Thus we see that the operator q carries the state into one of lower energy, the difference in energy being hv. If Φ_0 is the lowest energy state, we must have $q\Phi_0 = 0$; hence $W_0 = 0$ by (52.16). Consequently the energy of the Nth state Φ_N is

$$W_N = Nhv. \tag{52.21}$$

[Using (52.16*a*), we should have obtained $W_N = (N + \frac{1}{2})hv$].

In a similar way we find that $\bar{q}$ carries Φ_N into Φ_{N+1}. It is easily seen to follow from (52.16) and the equation

$$W\Phi_{N+1} = (N + 1)hv\Phi_{N+1}$$

that

$$(\bar{q}_{N+1N}q_{NN+1})^{1/2} = \bar{q}_{N+1N} = q_{NN+1} = \left[(N + 1)\frac{hv}{2\omega^2}\right]^{1/2}. \tag{52.22}$$

Creation and Annihilation Operators

The operators $\bar{q}$ and q will henceforth be referred to as the *creation* operator and *annihilation operator*, respectively. A discussion of these quantities would appear to be desirable at this stage.

If the cosine part of $e^{i\mathbf{kr}}$ in (52.13) is considered separately, we may put

$$\begin{aligned} Q &= q + \bar{q}, & P &= -i\omega(q - \bar{q}), \\ q &= \frac{1}{2}\left(Q + \frac{iP}{\omega}\right), & \bar{q} &= \frac{1}{2}\left(Q - \frac{iP}{\omega}\right), \end{aligned} \tag{52.23}$$

and thus obtain, because of the commutation rule

$$PQ - QP = \frac{h}{2\pi i},$$

the expression

$$W = \tfrac{1}{2}(P^2 + \omega^2 Q^2) - \tfrac{1}{2}h\nu. \tag{52.24}$$

Apart from the term $-\frac{1}{2}h\nu$ this is the Hamiltonian for a harmonic oscillator. Its matrix elements—and thus also the energy—are most easily found (as is well-known) by introducing the operators (52.23); the values

$$Q_{N+1N} = Q_{NN+1} = \left[(N+1)\frac{h\nu}{2\omega^2}\right]^{1/2} \tag{52.25}$$

then follow from (52.22) and (52.23).

Considering a sine oscillation we may obtain the form (52.24) by writing

$$Q = i(q - \bar{q}), \qquad P = \omega(q + \bar{q});$$

the resulting q and $\bar{q}$ then differ from those in (52.23) only by the factors $-i$ and i.

The operators q and $\bar{q}$ in (52.23) are annihilation and creation operators for standing cosine or sine oscillations. In (52.22) we may regard them as the corresponding operators for progressive unidirectional waves.

Interaction of the Quantized Field with Atoms

For simplicity we only consider a one-electron system, with the unperturbed Hamiltonian

$$H^0 = \frac{1}{2m_0}\mathbf{p}^2 + V. \tag{52.26}$$

When the atom is in an electromagnetic field, we must replace $\mathbf{p}$ by $p + (e/c)\mathbf{A}$. Thus we have for the entire system of atom + field the Hamiltonian

$$\begin{aligned} H &= H^0 + W + H', \qquad & H' &= H_1' + H_2', \\ H_1' &= \frac{e}{m_0 c}\sum_s \mathbf{A}_s\mathbf{p}, & H_2' &= \frac{e^2}{2m_0c^2}\sum_{ss'}\mathbf{A}_s\mathbf{A}_{s'}; \end{aligned} \tag{52.27}$$

here $W = \sum_s W_s$ is the total field energy, and $H' = H_1' + H_2'$ the interaction energy between the atom and the field. In contrast to our previous practice, we must not here omit the last (quadratic) term in $\mathbf{A}$, since this term now yields the contribution to the scattering that we formerly obtained in the semiclassical treatment from the last term in the current vector

$$\mathbf{j} = -\frac{c}{m_0}\operatorname{Re} u^*\left(p + \frac{e}{c}\mathbf{A}\right)u. \tag{52.28}$$

On the other hand, H_1' corresponds to the contribution formerly obtained from the first term in $\mathbf{j}$, that is, to the resonance terms in the dispersion formula.

The two parts of the interaction energy may be expressed in terms of the oscillator amplitudes as follows:

$$\begin{aligned} H_1' &= \sqrt{4\pi}\,\frac{e}{m_0}\sum_s (q_s e^{\mathbf{k}_s\mathbf{r}} + \bar{q}_s e^{-i\mathbf{k}_s\mathbf{r}})(\mathbf{e}_s\mathbf{p}) \\ H_2' &= \frac{2\pi e^2}{m_0}\sum_{ss'} (q_s e^{i\mathbf{k}_s\mathbf{r}} + \bar{q}_s e^{-i\mathbf{k}_s\mathbf{r}})\cdot(q_{s'} e_i^{i\mathbf{k}_{s'}\mathbf{r}} + \bar{q}_{s'} e^{-i\mathbf{k}_{s'}\mathbf{r}})(\mathbf{e}_s\mathbf{e}_{s'}). \end{aligned} \tag{52.29}$$

Calculation of the Matrix Elements for Quantum Transitions

We have previously, in (48.4) and (48.7), calculated the transition probabilities for direct and indirect quantum transitions; if these two processes occur simultaneously, the two formulas must, of course, be contracted to one. For reasons that will become apparent we replace E by E' and write

$$w_{mn} = \frac{4\pi^2}{h} N_m(E_n') \left| H_{mn}' - \sum_i \frac{H_{mi}' H_{in}'}{E_i' - E_n'} \right|^2. \tag{52.30}$$

Our primary task is therefore to calculate the matrix elements for the various quantum transitions. Once again we emphasize that the energy law $E_m' = E_n'$ must be valid for direct transitions $n \to m$, but not necessarily for the intermediate states $E_i' \neq E_m', E_n'$. In (52.30) E' is no longer the energy of the atom only, but the sum of the energies of the atom and field. The energy balance is upheld by absorption or emission of photons or by changes in the energy of the photons, for example, by incoherent scattering.

Let us in general denote a state of the entire system (atom + radiation field) and the corresponding energy by

$$\begin{aligned} \psi_{nN} &= \prod_s \Phi_{N_s}(q_s)\Psi_n(\mathbf{r}), \\ E_{nN} &= \sum_s N_s h\nu_s + E_n, \end{aligned} \tag{52.31}$$

where E_n is the energy of the atom, while the first sum is the photonic energy of the excited proper oscillations of the field. If the transition consists of, say, the disappearance of a photon $h\nu_s$, the energy balance may be expressed as

$$E_m = E_n + h\nu_s, \tag{52.32}$$

where E_m is the energy of the atom in the new state $\Psi_m(\mathbf{r})$.

Strictly speaking, our general matrix elements should be written

$$H'_{mM,nN} = \int \psi^*_{mM} H' \psi_{nN} \, d\tau \, d\tau_q, \tag{52.33}$$

where $d\tau_q$ is the element of volume in the coordinate space of all oscillator amplitudes, that is, $\prod_s dq_s$. However, it follows from (52.29) that the matrix elements are essentially those for the operators q_s and $\bar{q}_s$. These are different from zero only for transitions $N_s \to N_s \pm 1$, leaving all other $N_{s'}$ unaltered. This simplifies matters considerably, since we need only discuss a small number of processes involving one (or a few) photons. By utilizing the known matrix elements for these photon transitions we may dispense with the eigenfunctions $\Phi_{N_s}(q_s)$ for the oscillator amplitudes in the following calculations.

53. APPLICATIONS OF THE QUANTUM-ELECTRODYNAMIC METHOD TO RADIATION PROCESSES

Absorption and Emission

We may classify the processes to be considered as first-order, second-order, and so on, according to the number of photon transitions involved. Thus absorption and emission are first-order processes, while scattering is a second-order process. We must then take the point of view that in a scattering process the incident photon is absorbed, and the scattered photon reemitted, by the atom. A somewhat more precise definition may be obtained by noting the dependence of the transition probability on the electronic charge; for first-order processes they are proportional to e^2, for second-order to e^4, and so forth.

Thus it follows from (49.29) that, for first-order processes, only the interaction energy H'_1 comes into play. Hence we may consider only one single oscillator q and omit the summation over s. We assume that the oscillator frequency is ν; because of the energy balance, we must then have, for absorption and emission, respectively,

$$E_m = E_n \pm h\nu, \tag{53.1}$$

where E_n and E_m are the energies of the atom in the initial and final states.

We now index the matrix elements for H'_1—or for simplicity, H'—only by m and n, corresponding to the atomic states Ψ_m and Ψ_n, thus obtaining

$$H'_{mn} = \sqrt{4\pi} \frac{e}{m_0} (e^{i\mathbf{kr}}\mathbf{ep})_{mn} q_{N-1N}, \qquad \text{(absorption)} \tag{53.2a}$$

$$H'_{mn} = \sqrt{4\pi} \frac{e}{m_0} (e^{-i\mathbf{kr}}\mathbf{ep})_{mn} \bar{q}_{N+1N}. \qquad \text{(emission)} \tag{53.2b}$$

Because of the energy balance (53.1) the quantity $k = 2\pi/\lambda$ will usually be so small that we may put $e^{i\mathbf{kr}} = 1$ for distances $|\mathbf{r}| = r$ within the atom; this yields the familiar momentum matrix elements $(\mathbf{ep})_{mn}$. In principle, however, it is important to note the factor $e^{i\mathbf{kr}}$ which indicates that the rule of pure dipole transitions for absorption and emission is not exactly valid.

Substitution of the known values for the q- and $\bar{q}$-matrix elements leads by (49.22) to

$$|H'_{mn}|^2 = \frac{e^2h}{m_0{}^2\omega}\,|(\mathbf{ep})_{mn}|^2 \cdot \begin{Bmatrix} N \\ N+1 \end{Bmatrix} = e^2h\omega\,|(\mathbf{er})_{mn}|^2 \cdot \begin{Bmatrix} N \\ N+1 \end{Bmatrix} \tag{53.3}$$

for absorption and emission, respectively; we have here utilized the relation

$$(\mathbf{ep})_{mn} = i\omega_{mn}m_0(\mathbf{er})_{mn}$$

and put $\omega_{mn} = \omega$. We shall now calculate w_{mn} in (52.30), and must then determine the function $N_m(E'_n)$ or for brevity, $N(E')$, since $E'_m = E'_n$.

This function denotes the number of states in the energy interval dE' around the given energy E' of the system. Considering photons emitted within a solid angle $d\Omega$, and denoting the momentum of the photons by $p = h\nu/c$, we shall have (for a unit volume)

$$N(E')\,dE' = \frac{p^2\,dp\,d\Omega}{h^3} = \frac{\nu^2\,d\nu\,d\Omega}{c^3} \tag{53.4}$$

or since $dE' = h\,d\nu$,

$$N(E') = \frac{\nu^2\,d\Omega}{hc^3}\,. \tag{53.4a}$$

This yields

$$w_{mn} = \frac{4\pi^2}{h}\,N(E')\,|H'_{mn}|^2 = \frac{\omega^3e^2\,d\Omega}{hc^3}\,|(\mathbf{er})_{mn}|^2 \cdot \begin{Bmatrix} N \\ N+1 \end{Bmatrix}. \tag{53.5}$$

This formula has been deduced for the case of emission, where the final state is characterized by the direction and energy of the emitted photons. It is easily seen, though, that the same factor must appear in the formula for absorption; in this case we let the initial states be indeterminate to some extent and calculate the number of states around the energy E' for photon directions within the solid angle $d\Omega$.

We may now sum over all solid angles and calculate the mean square of the matrix element which we put equal to $\frac{1}{3}\,|\mathbf{r}_{mn}|^2$. Allowing, furthermore, for the fact that we have two independent polarization directions, we obtain altogether a factor $8\pi/3$. Finally we may take into account that most of the partial oscillations are not excited: As a rule we have $N = 0$, rarely $N = 1$, and practically never $N > 1$. Hence we may replace N by a mean quantum number

$\bar{N}$ and arrive at the formula

$$\bar{w}_{mn} = \frac{4\omega^4 e^2}{3c^3 h\nu} |\mathbf{r}_{mn}|^2 \cdot \begin{Bmatrix} \bar{N} \\ \bar{N}+1 \end{Bmatrix} \tag{53.6}$$

for absorption and emission, respectively.

It follows that the total transition probability for absorption in a radiation field is proportional to $\bar{N}$, and thus to the mean energy density $u(\nu)$ around the frequency $\nu = \nu_{mn}$. Since the number of oscillators in this frequency region is $8\pi\nu^2/c^3$, and the energy of each is $\bar{N}h\nu$, we have

$$u(\nu) = \frac{8\pi\nu^2}{c^3} \bar{N}h\nu. \tag{53.7}$$

In the case of emission we find an exactly analogous term which is also proportional to $\bar{N}$ or $u(\nu)$, and hence represents the induced emission. However, an additional term also appears [due to the factor $\bar{N} + 1$, instead of $\bar{N}$, in the last expression (53.6)] which is independent of the radiation density. This term is readily recognized as the previously mentioned transition probability for spontaneous emission which we have hitherto been unable to justify in a satisfactory manner. The Einstein coefficient for spontaneous emission is then

$$A_{nm} = \frac{4\omega^4 e^2}{3c^3 h\nu} |\mathbf{r}_{mn}|^2, \tag{53.8}$$

and the intensity of spontaneous radiation per atom is

$$I_{nm} = h\nu A_{nm} = \frac{4\omega^4 e^2}{3c^3} |\mathbf{r}_{mn}|^2. \tag{53.8a}$$

The coefficients $B_{mn} = B_{nm}$ are found by dividing the first expression (53.6) by $u(\nu)$; canceling $\bar{N}$, we thus obtain

$$B_{mn} = \frac{A_{nm}}{8\pi\nu^2 h\nu/c^3} \tag{53.9}$$

in agreement with the assumption that Einstein had to make in his deduction of Planck's radiation law (7.5).

Finally we may introduce the earlier mentioned oscillator strengths (43.9)

$$f_{mn} = \frac{4\pi}{h} m_0 \omega_{mn} |x_{mn}|^2 = \frac{4\pi}{3h} m_0 \omega_{mn} |\mathbf{r}_{mn}|^2, \tag{53.10}$$

to obtain for the mean absorption,

$$\bar{\eta}_a = \omega_{mn} h\nu = \frac{8\pi^2\nu^3 e^2 h}{c^3 m_0} f_{mn} \bar{N} = \frac{\pi e^2}{m_0} f_{mn} u(\nu). \tag{53.11}$$

This equation agrees with (5.10), except that the oscillator strength f_{mn} is not unity, but may take various smaller values.

Coherent and Incoherent Scattering of Short-Wave Radiation

We shall now consider second-order processes. The last term H_2' in (52.29) may give rise to a direct transition from an atomic state Ψ_n to Ψ_m. On the other hand, the first term H_1' will only be able to produce a transition through intermediate states Ψ_i, which necessitates a second-order perturbation calculation. Hence we shall consider the contribution of H_2', that is, direct transitions, first.

Since H_2' contains products of pairs of oscillator amplitudes, we shall have nonvanishing matrix elements only when two field oscillators both change their quantum number by unity. This may signify that two light quanta are both emitted or absorbed simultaneously, or that one is absorbed and the other emitted. We shall here discuss only this latter case which corresponds to an ordinary coherent or incoherent scattering, according as $m = n$ or $m \neq n$.

First of all, we utilize the fact that the radiation density in a scattering process may be regarded as very low, so that we need only consider the oscillator quantum number $N = 0$ and $N = 1$. In the initial atomic state Ψ_n we then have, say, an $N_s = 1$ and an $N_{s'} = 0$; while, in the final atomic state Ψ_m, these quantum numbers have changed to $N_s = 0$ and $N_{s'} = 1$. Thus we only have to deal with products of matrix elements

$$2q_{s01}q_{s'10} = \frac{h}{2\pi\sqrt{\omega\omega'}}. \tag{53.12}$$

We denote polarization, vectors and wave number vectors by $\mathbf{e}$, $\mathbf{e}'$ and $\mathbf{k}$, $\mathbf{k}'$, and put $\mathbf{k} - \mathbf{k}' = \mathbf{K}$. Using (52.29) we then find, as a first result,

$$(H_2')_{mn} = \frac{hc^2}{\sqrt{\omega\omega'}} r_0(\mathbf{ee}')(e^{i\mathbf{Kr}})_{mn}, \qquad r_0 = \frac{e^2}{m_0c^2}. \tag{53.13}$$

In order to determine the transition probability w_{mn} we must by (52.30) square the expression (53.13), and then multiply by

$$\frac{4\pi^2}{h} N(E') = \frac{\omega'^2\, d\Omega}{h^2c^3}, \tag{53.14}$$

since by (53.4*a*),

$$N(E') = \frac{\nu'^2\, d\Omega}{hc^3}.$$

This yields

$$w_{mn} = c\frac{\omega'}{\omega} r_0^2\, d\Omega\, |(\mathbf{ee}')(e^{i\mathbf{Kr}})_{mn}|^2. \tag{53.15}$$

However, this transition probability does not refer to one single photon but to the number of incident photons per second when the density is unity, corresponding to the fact that its dimension is volume · $\sec^{-1}$. This number is equal to c, so that we must divide by $c\,d\Omega$ to obtain the differential cross section

$$\sigma(\vartheta) = \frac{\omega'}{\omega} r_0^2 \,|(\mathbf{ee}')(e^{i\mathbf{Kr}})_{mn}|^2. \tag{53.16}$$

This formula is valid for both coherent and incoherent scattering of short-wave radiation. Its main ingredients are the classical electron radius r_0, the Thomson factor $(\mathbf{e} \cdot \mathbf{e}')$, and the atomic form factor $(e^{i\mathbf{K}\cdot\mathbf{r}})_{mn}$ for coherent and incoherent scattering.

The Complete Scattering Formula

Our calculation of the second-order perturbation of the term H_1' in (52.29) will be considerably simplified if we take advantage of the preceding computations of numerical factors. The first factor in (52.30) is evidently the same. The squaring of H_1' in (52.29) introduces a factor $2/m_0$ times the factor for H_2'; however, this is reduced to $1/m_0$, since the same term appears twice in H_2'.

In this second-order perturbation we shall, moreover, only consider transitions where one photon is absorbed and one emitted, that is, an ordinary scattering process. We have then to combine an annihilation operator q_s with a creation operator $\bar{q}_{s'}$.

It is to be noted that the order in which the two operators appear is crucial for the question of whether we, in the intermediate state Ψ_i of the atom, are to have two photons or none. More precisely, we have

$$E_n' = E_n + h\nu, \qquad E_i' = \begin{Bmatrix} E_i \\ E_i + h\nu + h\nu' \end{Bmatrix}, \qquad E_m' = E_m + h\nu',$$

that is,

$$E_i' - E_n' = \begin{Bmatrix} E_i - E_n - h\nu \\ E_i - E_n + h\nu' \end{Bmatrix}. \tag{53.17}$$

Employing the same designations as in (53.13) for polarization and wave number vectors, the complete scattering formula will read

$$\sigma(\vartheta) = \frac{\nu'}{\nu} r_0^2 \,|(\mathbf{ee}')f_{mn}(K) - g_{mn}(\mathbf{k}, \mathbf{k}')|^2,$$

$$g_{mn}(\mathbf{k}, \mathbf{k}') = \sum_i \frac{1}{m_0}\left[\frac{(e^{-i\mathbf{k}'\mathbf{r}}\mathbf{e}'\mathbf{p})_{mi}(e^{i\mathbf{kr}}\mathbf{ep})_{in}}{E_i - E_n - h\nu} + \frac{(e^{i\mathbf{kr}}\mathbf{e}'\mathbf{p})_{mi}(e^{-i\mathbf{k}'\mathbf{r}}\mathbf{ep})_{in}}{E_i - E_n + h\nu'}\right], \tag{53.18}$$

in agreement with (44.39).

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